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XII.—THE SWAN BAND SPECTRUM OF CARBON.

By W. E. Pretty, *A.R.C.S.*, *B.Sc.*, Demonstrator in Physics, Imperial College of Science, South Kensington.

Received December 24, 1927.

(*Communicated by* Prof. A. Fowler, F.R.S.)

Abstract.

The Swan spectrum has been obtained in carbon monoxide and in the carbon spark in the absence of hydrogen. A discussion of the results of experiment and theory leads to the conclusion that the emitter of the Swan band system is the molecule of carbon C_2.

Introduction.

THIS well-known spectrum, which predominates in the blue base of a bunsen flame, was first discovered by Wollaston in 1802, and independently in 1857 by Swan, from whom it receives its name. Since then the origin of the spectrum has been the subject of numerous investigations and speculations. These have been reviewed by Watts,* and only a brief summary need be given here.

The spectrum has been variously attributed to (i) a hydrocarbon, (ii) an oxide of carbon, (iii) carbon. Swan himself suggested acetylene as the emitter, and this view was adopted by Ångström and Thalén (1875). For the carbon-oxygen origin carbon monoxide has usually been specified, and has found supporters in Baly† and Smithells.‡ Among those who have favoured a purely carbon origin mention should be made of Attfield (1862-75), Dibbits (1864), Wullner (1872), Secchi (1873), Deslandres (1888), Eder (1890), La Rosa (1911), and Kayser (Handbuch der Spectroscopie, Vol. V, p. 206, 1910). From their earlier experiments, Liveing and Dewar, in agreement with Ångström and Thalén, were led to attribute the spectrum to acetylene, though the origin of the Swan spectrum was not the primary object of their investigation. Later,§ however, when giving special attention to this spectrum, they abandoned the view that hydrogen was essential to the production of the spectrum.

In spite of the enormous amount of work done on the subject, there has hitherto been no general agreement as to the origin of the Swan spectrum, and the question has recently been reopened by the work of R. C. Johnson.‖ From an analysis of the bands, and from a critical discussion of his own and other experimental work, Johnson has concluded that the emitter of the Swan band spectrum is a hydrocarbon.

The present investigation was undertaken with a view to submitting this conclusion to further experimental tests.

* Watts, Phil. Mag., Vol. 28, p. 117 (1914).
† Baly, "Spectroscopy," Vol. II, p. 220 (1927).
‡ Smithells, Phil. Mag. (i), p. 476 (1901).
§ Proc. Roy. Soc., 34, p. 418 (1882).
‖ Phil. Trans. Roy. Soc., A, Vol. 226, pp. 157-230 (1926).

EXPERIMENTAL.

Two methods of producing the spectrum were employed.

(i) Discharge through carbon monoxide at low pressure.

(ii) Carbon spark in various gases at atmospheric pressure.

It is well known that when an electric discharge is passed in carbon monoxide at a suitable low pressure the Swan spectrum is yielded brilliantly, and is often accompanied by traces of the hydrocarbon band at $\lambda 4315$, and by lines of hydrogen. The object in these experiments on carbon-monoxide was, therefore, to prepare the gas as free from hydrogen impurity as possible, and to examine the effect of such purification on the production of the Swan spectrum.

To this end the apparatus was made entirely of glass. The flask in which the gas was generated had a glass funnel fused into the neck, as shown in the diagram (Fig. 1). The electrodes were of thick platinum wire sealed into the limbs of the discharge tube. To facilitate the sealing in of the electrodes, the limbs of the discharge tube were made of lead glass. The discharge tube itself was of the ordinary H-pattern, having a capillary about 8 cms. long and 1 mm. in diameter. A pal-

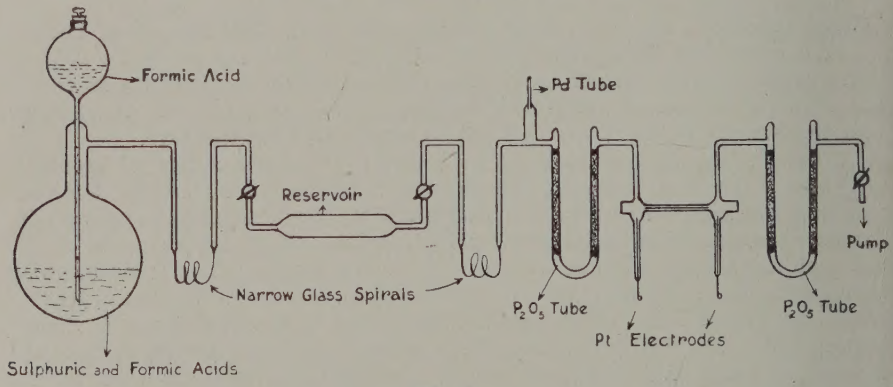


FIG. 1.

ladium tube was sealed on to the apparatus for the purpose of introducing or removing hydrogen as should be desired. With the apparatus so constructed the only source of hydrocarbon impurity was the small amount of grease used to lubricate the taps; but as these were well removed from the discharge tube it is very improbable that any grease could have reached the latter. The carbon monoxide was prepared by the action of pure sulphuric acid on pure formic acid (A.R. standard). From the generator the gas passed into a reservoir, where it could be stored when necessary. It was then passed through a U-tube containing phosphorus pentoxide to the discharge tube, and was exhausted through another U-tube containing phosphorus pentoxide.

The apparatus was first filled with carbon monoxide, then exhausted to a very low pressure, and a discharge passed for some time. This process was repeated several times to remove any impurities in the electrodes or on the walls of the apparatus. It was then left for a considerable time in order that any water present

might be absorbed by the phosphorus pentoxide. The presence of water in the carbon monoxide itself was not to be expected, as the gas was prepared from pure concentrated sulphuric and formic acids, and was therefore dried before leaving the generator. For the excitation of the tube an induction coil giving a 6″ spark in air was used; condensers, a variable inductance and spark gap being introduced into the circuit when required. The photographs were taken on a single prism instrument having a dispersion of about 5 *A* per mm. at λ4000 and 18 *A* per mm. at λ5700.

Various types of discharge were employed. With a spark gap and fairly large inductance in series, and condenser in parallel, the only spectrum seen was that consisting of the Swan bands. On reducing the amount of inductance the band system became relatively weaker, and lines due to carbon and oxygen made their appearance. Finally, when all the inductance was cut out, only the line spectrum remained. Some of these photographs are shown in Plate I. The pressure of the gas in these experiments was of the order of a few mms. of mercury. When the pressure of the gas was reduced the Ångstrom bands appeared, and eventually replaced the Swan bands, particularly with an uncondensed discharge.

The striking result from this part of the investigation was that not one of the very many photographs taken showed the least trace of the hydrogen line spectrum or of the hydrocarbon band at λ4315.

Hydrogen was next introduced into the apparatus by means of the palladium tube, and a discharge passed through the mixture of carbon monoxide and hydrogen. As was expected, the hydrogen lines Hα, Hβ appeared, together with the hydrocarbon band; the intensity of the Swan spectrum, however, was not appreciably changed.

A discharge was next passed continuously through the mixture of carbon monoxide and hydrogen, observations being made with a direct vision spectroscope. After a short time the hydrogen lines became fainter and the pressure decreased. Eventually the hydrogen lines disappeared, and a photograph taken with the tube in this condition showed no trace of the hydrogen lines or hydrocarbon band. By admitting further amounts of hydrogen the pressure was lowered sufficiently for the Ångstrom bands to replace the Swan system almost entirely. The explanation of this is, no doubt, that the hydrogen was oxidised to water by oxygen from the carbon monoxide, the water so formed being absorbed by the phosphorus pentoxide with considerable lowering of the pressure. The liberated carbon was deposited in a finely divided state on the walls of the discharge tube.

These experiments showed that the Swan spectrum could be obtained in carbon monoxide free from hydrogen to the extent that the latter could not be detected. Also, since hydrogen, which had been intentionally introduced, had disappeared during the passage of the discharge, it would appear highly improbable that traces of hydrogen impurity, if such had been present during the experiments on pure carbon monoxide, could have persisted for the many hours during which the different photographs of the Swan spectrum were taken.

Experiments on the Carbon Spark.

In order to vary the mode of production of the spectrum, a spark was passed between carbon poles in different gases, free, as far as could be obtained, from

hydrogen impurity. In this case the surrounding medium was at atmospheric pressure.

The carbon poles were about 5 mms. long and 2-3 mms. in diameter, and were supported by platinum leads, the distance between the poles being about 2 mms. The object of making the poles as small as practicable was to minimise the amount of any gases which might be evolved during the passage of the spark. The tube containing the poles was made of glass about 15 cms. long and 3 cms. in diameter. The first gas used was argon. This was passed over heated calcium (to remove hydrogen and nitrogen), through a long tube containing phosphorus pentoxide, and thence to the sparking tube. With a condenser and inductance included in the circuit, the Swan spectrum was readily obtained, together with the brighter bands of cyanogen, indicating nitrogen impurity. There was, however, no visible trace of hydrogen. The inductance was then cut out, and a photograph taken under these conditions showed a faint Hα.

On repeating the experiment with nitrogen (the calcium tube having been removed) a similar result was obtained, except that the cyanogen bands were relatively stronger than the Swan bands. This is not surprising, as the excitation potential for the CN bands is probably lower than that for the Swan system.

In an endeavour to remove the hydrogen impurity the spark was passed in air, and in this case the phosphorus pentoxide was contained in the spark tube itself, instead of in a separate tube. At first the result was the same as for argon and nitrogen ; but after continued running of the spark the hydrogen disappeared, no trace of it being seen on the plates even when the inductance was cut out and the line spectrum thereby obtained (Plate I (*f*)). As in the case of carbon monoxide, continued passage of the spark had brought about the oxidation of the hydrogen with formation of water, which had then been absorbed by the phosphorus pentoxide. In all cases the Swan spectrum was yielded, and the removal of the last trace of hydrogen did not affect in any way the intensity or appearance of the bands.

The evidence obtained from these experiments on the carbon spark is in agreement with that obtained from the experiments on carbon monoxide—that the Swan spectrum can be obtained in the absence of hydrogen.

Discussion of Results.

Among the chief experimental investigations which appear to show that oxygen is not necessary to the production of the spectrum are those of Watts* on the passage of sparks under carefully purified liquid carbon compounds. In heptane, hexane, octane and carbon tetrachloride the Swan bands were consistently observed. Similar results were obtained by Konen. Prof. Fowler has also informed the author that he has several times made similar experiments with benzene which had been boiled for several hours with sodium in a reflux condenser, and that he always found the Swan bands to be very bright when the spark was passed.

The earlier experiments on the appearance of the Swan bands in burning hydrocarbons, and in the carbon arc burning in hydrogen, clearly do not afford conclusive evidence that both hydrogen and carbon are necessary for the production of the bands. R. C. Johnson,† however, has described a new series of experiments which

* Watts, loc. cit.
† R. C. Johnson, loc. cit.

have led him to the conclusion that the emitter is a hydrocarbon, and from additional theoretical considerations he specifies in particular a molecule of the form HC-CH. Briefly these results were as follows: A discharge was passed between carbon electrodes in argon at about 30 mms. pressure, the discharge tube being of the ordinary H-type having a capillary about 20 cms. long and 1 mm. in diameter. When hydrogen was admitted to the tube the Swan spectrum was yielded brilliantly. A palladium tube was then heated to remove the hydrogen, and the Swan system grew fainter and finally disappeared, leaving only the continuous spectrum of high pressure argon, together with a few lines of the line spectrum of red argon. As hydrogen was readmitted the Swan bands reappeared. From these results it was concluded that hydrogen is essential to the production of the Swan spectrum; and, further, since only hydrogen and carbon were present, apart from argon, the origin of the spectrum must be hydrocarbon.

From the results of the experiments carried out in the present investigation, however, it would appear that the emitter cannot be a hydrocarbon. Also, since the Swan spectrum can be obtained in hydrocarbons free from oxygen, the only conclusion consistent with the results of experiment is that the emitter is purely carbon. On this view, Johnson's experiments may possibly be interpreted as follows: In the case of a discharge between carbon electrodes in pure argon the production of the Swan spectrum will depend on the presence of some agent which will enable the carbon to be freed from the poles and then be excited in the tube. In the complete absence of such an agent the discharge becomes such as would result if any electrodes other than carbon were used in pure argon, yielding only the continuous spectrum of argon together with some line spectrum. When, however, hydrogen is admitted, the carbon first forms a hydrocarbon, which is then excited and decomposed in the tube, the Swan spectrum being yielded by the carbon during the time that it is in the free state. According to this suggestion, it follows that a similar result would have been obtained by the admission of any other active gas, the function of the gas introduced being merely to bring about the conditions necessary for the carbon to be appropriately excited. Johnson admitted oxygen from a side bulb containing $KMnO_4$, and the Swan system appeared; but as the oxygen admitted contained sufficient hydrogen for the triplet system* (attributed by Johnson to a hydrocarbon) also to appear, it affords no test of the suggestion made above.

If a C_2H_2 origin is assumed, it is to be expected that there would be dissociation, to a greater or lesser extent, to CH and H; for this is certainly true of the higher hydrocarbons (Plate I (*a*)). In the author's experiments on CO no trace of the CH band or of the hydrogen line spectrum was seen on any of the plates, although hydrogen was readily indicated when it was intentionally introduced. Further, in order to account for the observed structure of the bands, Johnson assumes that the C_2H_2 emitter is of the form HC-CH, the binding in each CH group being sufficient to permit of its being treated as a single nucleus. In view of the fact that the CH molecule is known to emit bands of two systems, $^2D \rightarrow {}^2P$ and $^2S \rightarrow {}^2P$ neat $\lambda 4300$ and $\lambda 3900$ respectively, it does not seem probable that in the case of a C_2H_2

* Merton and Johnson, Proc. Roy. Soc. A, Vol. 103, p. 390 1923).

emitter the binding would be sufficiently close to permit of the CH group being treated as though there were no internal oscillation or rotation.

The Swan bands are found to consist of a triplet *P* branch and a triplet *R* branch, but no *Q* branch has yet been detected. The absence of a *Q* branch is taken by Johnson to indicate a high degree of symmetry in the emitting molecule. This assumption does not appear to be justified, for although *Q* branches have not been found for the symmetrical molecules N_2 and O_2, they are strongly developed in He_2. Also the *Q* branch is absent, or at any rate very weak, in systems due to CuH and CaH, and in the violet system of CN. These molecules are certainly not symmetrical. The apparent absence of or the presence of a very weak *Q* branch appears to be characteristic of systems which are due to transitions between like electronic states—e.g., CuH, $^1S \rightarrow {}^1S$; CN (violet) $^2S \rightarrow {}^2S$; NO β bands recently assigned to a $^2P \rightarrow {}^2P$ transition.*

The component lines of the triplets in the Swan bands show alternations of intensity which, up to the present, have been found only in systems known to be due to diatomic molecules composed of like atoms—e.g., N_2, N_2^+, O_2 and He_2. Hund† has recently interpreted the "Second Positive" band-system of N_2 as a $^3P \rightarrow {}^3P$ transition. Mulliken‡ has extended this to the Swan bands, and explains the apparent absence of a *Q* branch, and also the alternating intensities in the triplets, pointing out the strong analogy with the "Second Positive" system of N_2. This evidence does certainly point to a symmetrical diatomic molecule as the emitter of the Swan bands.

Johnson has analysed the structure of the bands, and finds that the moment of inertia of the emitter is of the same order as that obtained for the molecules CO, N_2 and O_2. Such a value would be given by a molecule of acetylene C_2H_2, assuming each CH group acted as a single nucleus, and also by a molecule composed of two carbon atoms C_2. The determination of the moment of inertia, therefore, while showing that both C_2H_2 and C_2 are of the right order, fails to decide between the two.

Experiment leads to the conclusion that the emitter is purely carbon. Theory indicates that the emitter is a symmetrical diatomic molecule. The molecule fulfilling these conditions, and also giving a value for the moment of inertia which is of the order obtained from an analysis of the structure of the bands, is the molecule of carbon C_2.

In conclusion, the author wishes to express his thanks to Prof. A. Fowler, at whose suggestion this investigation was undertaken, for his continued interest and advice during its progress.

Note Added January 25, 1928.

Since the completion of the above investigation a paper on the "Structure of the Swan Bands," by J. D. Shea,§ has appeared, in which the opinion is expressed that the carrier is a purely carbon molecule; either C –C or, if such a combination can exist, $C^- - C^-$.

* Jenkins, Barton and Mulliken, Phys. Rev., Vol. 30, p. 150 (1927).
† Hund, Zeits. f. Phys., 36, p. 657 (1926).
‡ Mulliken, Phys. Rev., Vol. 29, p. 637 (1927).
§ Shea, Phys., Rev., Vol. 30, p. 825 (1927).

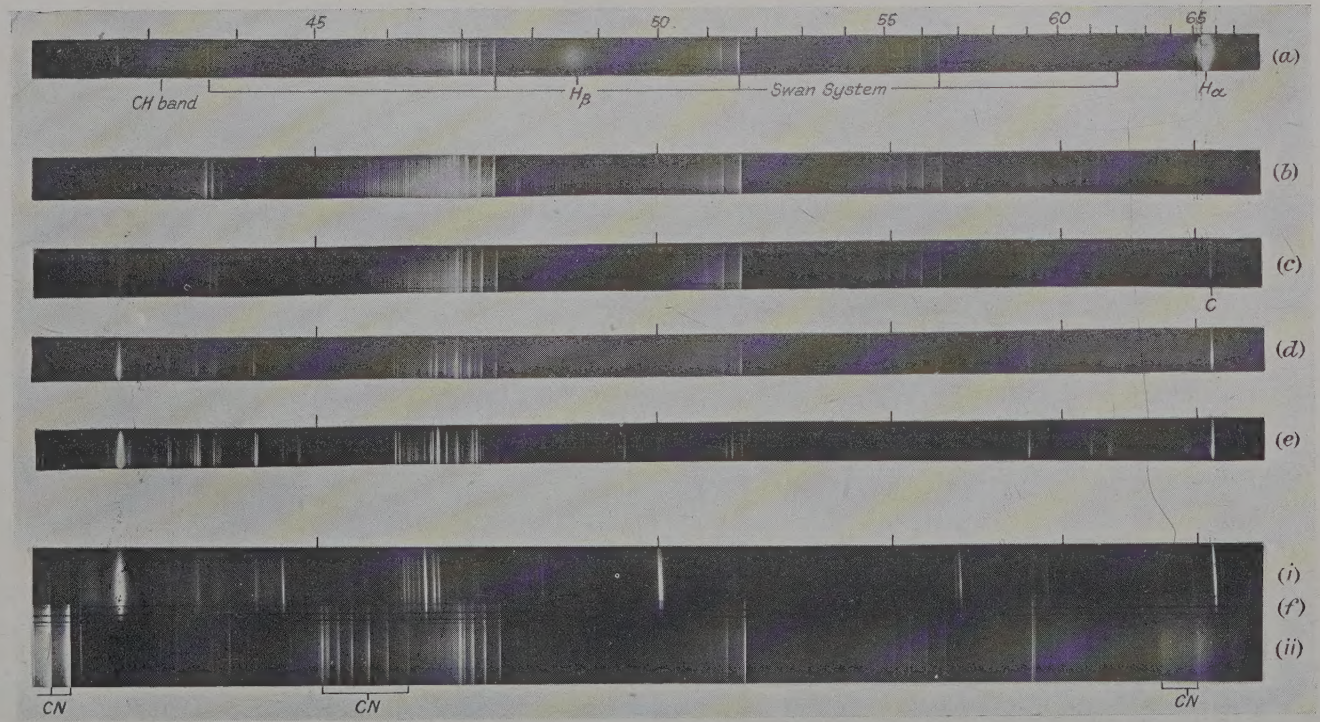


PLATE I.—PHOTOGRAPHS OF THE SWAN SPECTRUM.

[To face page 77

Description of Plate I.

(*a*) Discharge through pentane (C_5H_{12}). Condenser and inductance, showing hydrogen lines and CH band in addition to Swan system.

(*b*), (*c*), (*d*), (*e*). Discharge through carbon monoxide. Condenser and diminishing inductance. (*b*) is a purely Swan spectrum; (*e*) shows lines of carbon and oxygen but no hydrogen; (*c*) and (*d*) are intermediate stages.

(*f*) Carbon spark in air.

(i) Condenser, no inductance; showing lines of oxygen, nitrogen and carbon, but no hydrogen.

(ii) Condenser and inductance; showing Swan system.

DISCUSSION.

Dr. R. C. Johnson said that, while the author's work was of great interest, he did not think that it justified the conclusion reached. The emission of the Swan band from carbon monoxide dried with P_2O_5 was a familiar occurrence, but he did not think that the absence of hydrogen could be assumed. The relative intensity of spectra depends more on the excitation potentials than on the percentage in which the components of a gas mixture are present. Thus a mere trace of a hydrocarbon in helium at a pressure of 40 mm. will drown the helium spectrum, owing to the relatively low excitation potential of the former. Mulliken, in the Physical Review, had recently pointed out that the molecules C_2, BN, BeO, LiF all have a similar outer structure; they are polar molecules of marked chemical stability, and are theoretically incapable of emitting band spectra, while extensive experimental research has hitherto failed to reveal band spectra in any of these cases, with the doubtful exception of BeO. Analogy, therefore, makes the C_2 origin of the Swan bands improbable, whereas the C_2H_2 molecule is similar in its external structure to N_2, which has two valency electrons and exhibits a band spectrum similar to the Swan spectrum. Again, if a gas jet be plentifully supplied with air the flame is blue, owing to the presence of the 4315 band of CH, whereas when the air supply is reduced the Swan spectrum appears and turns the flame green; this result may be attributed to the association of 2CH into C_2H_2, which may be regarded as a rotating dipole HC–CH. Shea had suggested $(C\text{-})_2$ as the Swan emitter, but there appeared to be no justification for the revolutionary assumptions involved in this suggestion, and such a structure, if it could exist, would not resemble the N_2 molecule. It was desirable to investigate the Swan absorption spectrum. Hori had obtained it by exploding by sudden heat a thread of mercury in a vacuum chamber which happened to contain hydrocarbon gases from the oil of a pump. It would be interesting to fuse the filament of a carbon-filament lamp, after exhausting the latter if necessary, and to see whether the absorption spectrum was obtained.

Prof. E. N. da C. Andrade pointed out that hydrogen would be occluded in the carbon of the lamp, and the speaker agreed that the result would be inconclusive.

Dr. W. Jevons: An experimental investigation as to the emitter of the Swan band system was perhaps one of the most urgent in molecular spectroscopy, and I tender my hearty congratulations to the author on the very thorough manner in which he has carried it out. His result will, I am sure, win immediate and general acceptance. It is unfortunate that Mr. Pretty's Paper did not appear, say, two months ago, for a very important Paper (Phys. Rev., 30, 825, December, 1927) has just been published by J. D. Shea, who has analysed the 0,0 (λ5165), 0,1 (λ5635), 1,0 (λ4737), 1,1 (λ5129), and 1,2 (λ5585) bands, and, like Mr. Pretty, has pronounced in favour of C_2 as the emitter, but has added a suggestion that it might be $(C\text{-})_2$. In a preliminary report of this work to the American Physical Society (Phys. Rev., 27, 245, abs. 14, 1926) Shea and Birge drew attention to the surprising similarity of the values obtained for the moments of inertia (I_0) and the electronic angular momentum (ε) of the emitters of the Swan system and the N_2 "Second Positive" system. And, since the acetylene molecule $(CH)_2$ has the same number of electrons and nearly the same mass as N_2, they thought that $(CH)_2$ *might* be the Swan emitter if it could vibrate and rotate as a dipole. The $(CH)_2$ suggestion, though supported in Dr. Johnson's Paper (which appeared shortly afterwards), was not acceptable to several practical spectroscopists who had very many years' experience as to the occurrence of the Swan bands, nor to the investigators who have done most to bring about the rapid development of the theory in the last twelve months. On the face of it, a tetra-atomic molecule like $(CH)_2$ was

unlikely to emit a band-system of the same simplicity as one emitted by the di-atomic molecule N_2. Mulliken has, as Mr. Pretty states, attributed the Swan bands to the transition $^3P \rightarrow {}^3P$ (or, less probably, $^3D \rightarrow {}^3D$) in the C_2 molecule ; and I might add that Prof. Mulliken informed me last summer that Hund had deduced that the Swan emitter has, like He_2, etc., zero nuclear spin —a result compatible with a pole like C, but not with one like CH. Shea and the author of the present Paper are, then, in agreement with Hund and Mulliken. Like Dr. Johnson, I have a difficulty in understanding why the Ne-like (no-valence-electron) molecule C_2 should emit a band-system of the same type as one emitted by Mg-like (two-valence-electron) molecule N_2. Shea's $(C^-)_2$ would remove the difficulty, *if* it could reasonably be assumed to exist in an electronically excited ^3P state, and also to be capable of vibration and rotation as a dipole. I would like to add a word about two other twelve-electron molecules BN and BeO, which Dr. Johnson mentions with C_2 as being improbable emitters. BN, for which my early argument was mostly based on analogy with CN and SiN in active nitrogen, is of course entirely withdrawn, as Dr. Johnson says, in view of Mulliken's unassailable evidence for BO as the emitter of the bands in question. I have quite recently started an investigation of the beryllium band-system described by Glaser, but I have done too little yet to decide whether BeO is its emitter. I cannot altogether agree with Dr. Johnson's statement that CH is incapable of vibration and emits only non-vibrational (0,0) bands. For, in addition to the twelve branches of the 0,0 band of the $^2D \rightarrow {}^2P$ system near λ4300 Hulthén (Dissertation, Lund, 1923) detected eleven fainter branches which Birge (National Research Council Bulletin, No. 57, p. 193, footnote 132) regards as possibly belonging to the 1,1 band of the same system.

Author's reply : I should like to point out to Dr. Johnson that the object in reducing the amount of inductance included in the circuit was to ensure that the discharge was sufficiently violent for hydrogen lines to appear if any of the gas were present. This is evidenced by the fact that the carbon doublet at λ6580 (excitation potential—16 volts) appeared very strongly. The calculated excitation potential for H_α is about 12 volts. Why the molecules C_2, BN, BeO and LiF should not be expected to radiate is not altogether clear, for the corresponding atom Ne is easily excited. The phenomena accompanying the change in a gas flame when the air supply is varied can be explained on a carbon hypothesis. With an insufficiency of air there is a greater proportion of carbon available. As the air supply is increased the carbon is oxidised to a greater extent, and is then incapable of yielding the Swan spectrum. I might point out that, according to Smithells, the flame of pure dry cyanogen in pure dry oxygen yields a brilliant Swan spectrum. This is very difficult to reconcile with a hydrocarbon emitter. Dr. Johnson attempts to justify the close binding of the CH group, which yields the systems at λ4300 and λ3900, by pointing out that only the non-vibrational (0,0) bands have been observed. Kratzer has analysed the two systems, and has calculated the values of the internuclear distance for the different electronic states. The smallest of these values is approximately the same as the value obtained by Johnson for the separation of the nuclei in the emitter of the Swan system. It cannot therefore be held that the binding in the CH group is close compared with that in the emitter of the Swan bands.

XIII.—THE ELECTRODELESS DISCHARGE THROUGH GASES.

The Thirteenth Guthrie Lecture, Delivered March 9, 1928.

By Sir J. J. Thomson, *O.M., F.R.S.*, Master of Trinity College, Cambridge.

BY "electrodeless discharge" I mean a discharge where the currents form closed circuits in the gas, and have not to pass from gas to metal, as in discharge tubes with metallic electrodes, or from gas to glass, as when metallic electrodes are placed outside the tube. This ring discharge can be produced by placing outside the bulb or tube containing the gas at a low pressure a solenoid placed in a circuit connecting the outsides of two Leyden jars. The insides of these jars are connected respectively with the two terminals of an induction coil; when sparks pass between these terminals, rapidly alternating currents, whose frequency is inversely proportional to the square root of the product of the capacity of the jars and the self-induction of the circuit, pass through the solenoid. The electromagnetic induction due to these currents starts in the exhausted vessel currents which flow in rings whose axis coincides with that of the solenoid.

Theory of the Discharge.

When the solenoid is long and straight, the theory of the discharge is as follows:

The tangential electric force at a point distant r from the axis of the solenoid is equal to

$$\frac{1}{2\pi r}\int_0^r \frac{dH}{dt}2\pi r\,.\,dr=\frac{1}{r}\int_0^r \frac{dH}{dt}r dr,$$

where H is the magnetic force at the distance r. The tangential force on a moving electron at r is therefore

$$e\left(\frac{1}{r}\int_0^r \frac{dH}{dt}r dr+H\frac{dr}{dt}\right)$$

$$=\frac{e}{r}\cdot\frac{d}{dt}\int_0^r Hr dr.$$

Hence, if m is the mass of the electron

$$m\frac{1}{r}\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right)=\frac{e}{r}\frac{d}{dt}\int_0^r Hr dr$$

or

$$mr^2\frac{d\theta}{dt}=e\int_0^r Hr dr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

if H and $d\theta/dt$ vanish simultaneously.

If there are no currents through the gas, or if these are very small compared

with those through the solenoid, as they will be while the discharge through the gas is being initiated, H will be independent of r, so that equation (1) gives

$$mr^2\frac{d\theta}{dt}=e\frac{Hr^2}{2}$$

or

$$\frac{d\theta}{dt}=\frac{1}{2}H\frac{e}{m}$$

thus all the electrons have the same angular velocity round the axis of the solenoid.

In order that the discharge should take place, the energy given to an electron must be great enough to enable it to ionise the gas—i.e., it must not be less than We if W is the ionising potential. If $W=\frac{1}{2}mw^2$, then the electron must acquire a velocity at least as large as w to enable it to start the discharge.

if $H=H_0 \sin pt$

$$\frac{d\theta}{dt}=\frac{1}{2}H_0\frac{e}{m}\sin pt$$

The maximum value of $d\theta/dt=H_0e/2m$.

If a is the radius of the discharge tube, whose axis is supposed to coincide with that of the solenoid, the maximum velocity of an electron is $aH_0e/2m$, and one condition for the discharge is that this velocity should not be less than w. The electron will not, however, acquire this velocity under the electric force if it makes a collision with the molecules of the gas before it attains it, for this would take away the energy it had already acquired. Thus the condition for the discharge is that the electron should acquire a velocity w before it has travelled over a distance λ, where λ is the free path of the electron through the molecules of the gas. The distance travelled by the electron is $a\theta$; since

$$\frac{d\theta}{dt}=\frac{1}{2}H_0\frac{e}{m}\sin pt$$

$$a\theta=\frac{1}{2}a\frac{H_0}{p}\frac{e}{m}(1-\cos pt)$$

Hence the condition for the discharge is that when

$$\frac{1}{2}aH_0\frac{e}{m}\sin pt=w$$

$$\frac{1}{2}a\frac{H_0e}{mp}(1-\cos pt)=\lambda$$

From these equations we get

$$a\frac{H_0e}{m}=\frac{w^2+(p\lambda)^2}{p\lambda} \quad \ldots\ldots\ldots\ldots \quad (2)$$

Hence H_0 is infinite when $p\lambda$ is either zero or infinity—i.e., when the pressure is infinite or when it vanishes, and H_0 will have a minimum value when $p\lambda=w$, and the minimum value of H_0 is $\frac{2m}{ae}w$.

Thus for the electrodeless discharge, as well as for the spark discharge between

electrodes, there is a critical pressure at which the spark passes most easily; the critical pressure for the electrodeless discharge depends on the frequency of the currents, and is directly proportional to this frequency; the critical pressure for the spark discharge depends upon, and is directly proportional to, the spark length.

The magnetic force required to produce the electrodeless discharge is a function of $p\lambda$, or p/P if P is the pressure, and does not alter as long as this is constant. We may compare this with Paschen's law for the spark discharge, according to which the potential required to produce the spark is a function of the product of the pressure and the spark length.

The electromotive force round a circuit of radius r in the discharge tube is

$$\pi r^2 \frac{dH}{dt}, \text{ i.e., } \pi r^2 p H_0 \cos pt$$

on substituting the value of H_0 from equation (2), we find that the E.M.F. round the circuit when the discharge is passing is

$$\pi r^2 p \cdot \frac{m}{ea} \frac{w^2 + (p\lambda)^2}{p\lambda} \cos pt$$

Thus the peak value of this has a minimum value when $p\lambda = w$, and the E.M.F. round the circumference of the tube is $\frac{2\pi a \cdot mw^2}{\lambda e}$.

In the non-striated uniform positive column in the discharge between electrode the electric force F at a point is given by the equation

$$Fe\lambda = \frac{mw^2}{2}$$

Hence the difference of potential in a length $2\pi a$ of the positive column—i.e., in a length equal to the circumference of the ring discharge—is $2\pi a \cdot F$—i.e.,

$$\frac{2\pi a \cdot mw^2}{2\lambda e},$$

This is one-half of the peak E.M.F. round the ring when the electrodeless discharge is passing most easily. A further analogy between the ring discharge and the positive column is that within certain limits of pressure and current density the electrodeless discharge, like the positive column, shows striations. These for the electrodeless discharge are much more conspicuous in hydrogen than in any other gas I have tried.

In hydrogen I find the electrodeless discharge sometimes has the appearance shown in Fig. 1. There are well marked striations, which, however, flicker about too much to allow of photographs being taken.

I have measured the E.M.F. round the bulb when the electrodeless discharge is passing at different pressures, and found that there is a minimum at a certain pressure; the minimum is, however, a very flat one, so that it is not possible to determine the critical pressure accurately. Experiments showed, however, that it was much higher for helium than for any other gas, and that it increased with the frequency of the alternating currents.

In the preceding investigation the currents through the gas have been assumed to be very small, as they will be when the discharge only just passes. When the spark-gap between the terminals of the induction coil is lengthened a very bright discharge passes through the gas, and the currents through it are comparable with those through the solenoid; the magnetic force, instead of being uniform over the cross-section of the tube, is now very much greater near the walls of the tube than it is near to the axis. Experiments showing this effect are described in the Phil. Mag. iv., p. 1128, 1927. When these large discharges pass through the gas there are many free electrons and positive ions distributed through the gas, and the pressure is generally so low that the motion of the electrons may be regarded as free, and not influenced by collisions with the molecules of the gas. The properties of a medium of this kind are exceedingly interesting and important. For example, the "Heaviside layer," which plays such an important part in the transmission of electrical waves, has this constitution, and the electrodeless discharge is a convenient method for investigating experimentally its properties.

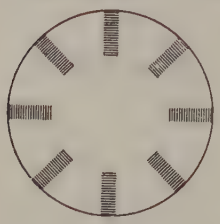


FIG. 1.

The theory of the electrical properties of such a medium is quite simple.

Let X, Y, Z be the components of the electric, α, β, γ those of the magnetic force; u, v, w the components of the electric currents in the gas, x_r, y_r, z_r, the co-ordinates fixing one of the electrons; c the velocity of light. Then the field equations are

$$u=\frac{1}{4\pi}c^2\frac{dX}{dt}+\Sigma e\,.\,\frac{dx_r}{dt}$$

With similar equations for v and w

$$m\frac{d^2x_r}{dt^2}=Xe$$

where m is the mass of an electron; we suppose that the current through the gas carried by the electrons is large compared with that carried by the positive ions.

The other equations are

$$4\pi u=\frac{d\gamma}{dy}-\frac{d\beta}{dz}$$

with similar equations for v and w

$$\frac{d\alpha}{dt}=\frac{dy}{dz}-\frac{dz}{dy}$$

with similar equations for $d\beta/dt$ and $d\gamma/dt$.

From these equations it follows that α, β, γ, X, Y, Z satisfy differential equations of the type

$$\frac{d^2\psi}{dt^2}+4\pi c^2\frac{Ne^2}{m}\psi=c^2\left(\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

when N is the number of electrons per unit volume. A vibration of frequency p and wave length λ will be represented by

$$\psi=\cos\left(pt-\frac{2\pi}{\lambda}(lx+my+nz)\right)$$

when l, m, n are the direction cosines of the normal to the wave front. Substituting this value of ψ in equation (3) we find

$$p^2=4\pi c^2\,.\,\frac{Ne^2}{m}+\frac{4\pi^2}{\lambda^2}c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If the gas is confined within a discharge tube, the possible values of λ will be determined by the boundary conditions, and will depend on the size and shape of the tube. The possible values of λ will be comparable in magnitude with the linear dimensions of the tube. To each value of λ will correspond a particular frequency p; but we see from equation (4) that whatever be the value of λ, p cannot be less than $c\sqrt{4\pi Ne^2/m}$. Thus the frequencies of the free vibrations of the gas will form a series with a definite lower limit. The ionised gas will thus have definite periods of vibration, and when the ionisation is very dense all these periods will cluster round the value $2\sqrt{4\pi Ne^2/m}$, and will be but little influenced by the size of the vessel. Thus we conclude that the ionised gas would emit vibrations—i.e., it would send out electrical waves—and that the greater the density of the ionisation the higher the frequency of the waves.

These results refer to the free vibrations excited in the gas. Let us now consider the forced vibrations due to the alternating current through the solenoid. If p is the frequency of these currents

$$\frac{d^2\psi}{dt^2}=-p^2$$

and for a plane wave travelling along the axis of x equation (3) becomes

$$\frac{d^2\psi}{dt^2}+4\pi\frac{c^2Ne^2}{m}\psi=c^2\frac{d^2\psi}{dx^2}$$

or

$$\left(4\pi c^2\,.\,\frac{Ne^2}{m}-p^2\right)\psi=c^2\frac{d^2\psi}{dx^2}$$

If p^2 is less than $4\pi c^2Ne^2/m$, the coefficient of ψ on the left-hand side is positive; hence ψ will not be represented by a harmonic, but by an exponential function of x, and the expressions for ψ will contain a term $\varepsilon^{-x/R}$

where

$$\frac{1}{R}=\sqrt{\left(4\pi\frac{Ne^2}{m}-\frac{p^2}{c^2}\right)}$$

So that a disturbance would die down to $1/t$ of its original value in a distance equal to $1/\sqrt{4\pi Ne^2/m-p^2/c^2}$. Thus no forced disturbance whose frequency is less than the critical frequency can travel as a wave through the gas; it only penetrates a distance equal to the value just found.

In our experiments the forced disturbances are magnetic forces spreading from

the solenoid through the ionised gas. When the ionisation is strong, the frequency of the alternating currents is small compared with the critical frequency, so that the magnetic force will only travel a distance measured by $1/\sqrt{4\pi Ne^2/m}$ into the gas. The experiments show the existence of this effect very plainly, for when the ionisation is very intense the discharge consists of a thin, very brightly luminous ring close to the surface of the discharge tube. The thickness of this ring enables us to form some idea of the intensity of ionisation, for since the light is very bright at the outer edge of the ring, and very faint at the inner one, the magnetic force must have fallen to much less than $1/\varepsilon$ of its value in a space equal to the thickness of the ring. Thus in an experiment in hydrogen, at a pressure of 1/50 of a millimeter of mercury, I estimated the thickness of the bright ring as about a millimeter; hence we must have

$$\frac{1}{\sqrt{4\pi Ne^2/m}} < 0{\cdot}1$$

or

$$4\pi Ne^2/m > 10^2$$

Now $e^2/m = 3\times10^{-13}$, hence N must be greater than $10^{15}/12\pi$. At a pressure of 1/50 of a mm. the number of molecules per cubic centimetre is about $0{\cdot}7\times10^{15}$. So that in this experiment the number of electrons must have been comparable with the number of molecules.

Effect of Light on the Electrodeless Discharge.

The electrodeless discharge supplies a very convenient means for studying the effect of various physical agents on the passage of the discharge through gases. The first example I shall take is the effect of light on the discharge.

It has been known for many years that the passage of a spark between electrodes is facilitated by exposing the spark-gap to light; this, however, is due to the photoelectric effect at the cathode producing a discharge of electrons which helps to start the discharge. In the experiments with the electrodeless discharge there are, of course, no electrodes, and precautions were taken to prevent the light striking against the glass walls of the tube in the neighbourhood of the ring discharge. The arrangement adopted is shown in Fig. 2.

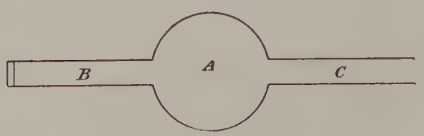


Fig. 2.

The ring discharge passes in the bulb A, two long tubes B and C connect with this bulb, and at the end of B there is a quartz window, and through this a parallel beam of light passes down the axis of the tube; the ends of the tubes B and C, which are far away from the bulb, are the only parts of the apparatus hit by the rays of light.

The length of the spark between the terminals of the induction coil is adjusted until, when the light is screened off, the ring discharge just ceases to pass through the gas. When the light is sent through the tube a ring discharge with considerable luminosity appears. The effect has been found in a great variety of gases, in air, hydrogen, helium, argon, oxygen, nitrogen, carbonic acid, iodine vapour and mercury vapour. It is not so apparent when the pressure is very low as at somewhat higher

pressures. The pressure at which the effect is a maximum depends on the nature of the gas ; it is higher for the lighter gases, like hydrogen and helium, than for the heavier ones. It is well developed in most gases at a pressure of about 0·1 mm. of Hg ; the range of pressure over which it exists is very considerable—e.g., I have observed the effect in air over a range of pressures from 0·007 to 7 mm.

The effect is produced by light from very varied sources, by light from a mercury lamp, from an arc lamp, from sparks between metallic terminals, and from the brush discharge. What is perhaps rather surprising is that the light from an ordinary spirit lamp is very effective, as is also the light from a Bunsen burner, or from the oxyhydrogen flame, especially the light coming from the luminous cone. The light from the electric discharge through a gas at low pressure is effective if the tube containing the gas is made of quartz, but not if it is made of glass.

It is essential for the success of the experiment that the light should not pass through anything opaque to ultra-violet light before going through the gas ; very thin films of glass or mica, or even of celluloid, are sufficient to destroy the effect, though it is not stopped when the light passes through plates of quartz or of rock salt several millimetres thick.

This effect does not show much evidence of selective absorption. We might, for example, have expected that when using the light from a mercury lamp the effect would be abnormally large when the ring discharge went through mercury vapour. To test this, I compared the relative effects produced by a mercury lamp and the arc light, (*a*) when the ring discharge passed through pure oxygen, and (*b*) when it passed through a mixture of oxygen and mercury vapour. The ratio of the effect in (*b*) to that in (*a*) seemed to be a little greater for the mercury lamp than for the arc, but there was not much difference.

In another experiment I used as the source of light a quartz tube filled with hydrogen ; this did not seem to produce abnormally large effects when the ring discharge passed through hydrogen.

The light does not by itself ionise the gas or produce a supply of free electrons. This was proved by measuring the rate at which negative electricity escaped from a metal plate placed in the bulb *A* (Fig. 2) out of the way of the light and when no ring discharge was passing ; the small leak due to residual ionisation was not increased by exposure to the light.

The effect of illumination on the ring discharge is evidently due to the absorption of ultra-violet light ; such absorption seems from the experiments just described to be a frequent accompaniment of the passage of light through gases. There would be such an absorption of ultra-violet light from a variety of sources by many different gases either if these sources gave out a continuous spectrum in the ultra-violet, or if the gases had continuous absorption in that region. The energy absorbed, though not sufficient to eject electrons from the atoms or molecules of the gas, may be sufficient to put these for a time, which is not infinitesimal, into a state in which they are more easily ionised than when they are normal. Thus, as the work of ionisation is already half done, the external electric field will not be called upon to supply as much energy to the free electrons to make them ionise these excited molecules as would be required to make them ionise normal atoms or molecules ; and thus the ring discharge will pass more easily when the gas is illuminated than when it is not.

Effect on the Ring Discharge of Impurities in the Gas.

I have observed some curious and suggestive effects produced by the presence of various substances in the gas. The kind of effect is illustrated by the following experiment. The discharge tube was a long cylindrical glass one, along which the solenoid carrying the alternating currents could be moved from end to end. A thin cylindrical glass rod AC ran along the axis of this tube, and on a portion B of this tube a thin layer of sulphur was deposited; the length of this deposit was about the same as that of the solenoid. When the solenoid did not encircle the rod, or when it encircled the part of it not covered by the sulphur, the ring discharge was very bright, but it stopped when the solenoid came over the part covered by the sulphur, and started again when the solenoid was moved away from this part. When the gas in the tube was either hydrogen, air or nitrogen there was a rapid diminution in the pressure, showing that chemical combination was going on; but the effect just described occurred also when the tube was filled with helium, when there was no diminution in the pressure.

With this rod in the tube it was found impossible, whatever might be the gas filling, to maintain the discharge for long, even though the solenoid did not encircle the sulphur. Though the discharge might be bright to begin with, it got fainter gradually, and finally disappeared. Sometimes it was found impossible to get the discharge to start again however much the spark-gap between the terminals of the induction coil was increased. If the tube was left for some hours, or if a current of gas was drawn through it for some minutes, it recovered its power of giving a

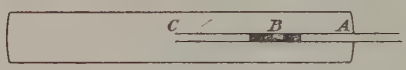


Fig. 3.

luminous discharge. The effect seems to be connected with a deposit on the walls of the tube, for if the tube be heated for some minutes with a gas flame it recovers its power of giving a bright discharge. If one half the tube has been heated while the other half has been left cold, the discharge will often pass when the solenoid is over the part which has been heated, but will not do so when the solenoid is over the other portion.

I have tested the effects produced by deposits of substances other than sulphur. Phosphorus produces a large effect, and appreciable effects are produced by deposits of silver, platinum, cadmium; the effect, if any, produced by graphite was much smaller than with the other substances.

The effect is most marked when the pressure of the gas is only a few hundredths of a millimetre, and gets much less at considerably higher pressures; it does not seem to depend on the nature of the gas, as it occurs in hydrogen, air, oxygen and helium. If after the discharge has been running for some time the tube is heated strongly in the neighbourhood of the place where the substance is deposited on the glass rod, it often happens that immediately after the heating the discharge will pass when the solenoid is over the patch of substance, the place where it was stopped before the heating, but that it is now stopped at some other part of the tube where it went before. This suggests that the effect is due to a deposit on the walls of the tube which is driven off when it is heated.

The following considerations help us to understand the retardation produced by substances like sulphur and phosphorus on the discharge. To start the discharge there must be some electrified bodies to begin with. In a gas in which there was nothing but neutral molecules it would be impossible to start the discharge unless the electric field were strong enough to tear the electrons out of the molecules; to do this would require a field of quite a different order of intensity from that in our discharge tubes.

It is to stray electrons that we must look for the initiation of the discharge. Under ordinary conditions there is always a certain amount of ionisation going on in the gas, but before an electron produced in this way can ionise the gas it has to get from the electric field energy greater than the ionising potential, and it has to convey this energy to an electron in a molecule before that electron can be liberated. When the electric field is not much more intense than the limit which will just produce discharge, it may be only one out of a very large number of collisions which will result in the transfer of a sufficient quantity of energy. Anything which reduces the life of the electron below the time necessary for it to make these collisions will reduce its efficiency for producing the discharge. The electron loses its power of ionisation when it unites with a molecule to form a negative ion. Loeb's experiments show that the number of collisions an electron makes with the molecules before it unites with one of them depends very greatly upon the nature of the gas. Thus, it is certainly many millions for pure nitrogen or helium, for oxygen in which the electron has a comparatively short life the number of collisions is about 30,000, while in chlorine it is less than 300. Thus, for the electronegative gases, the number of collisions is exceptionally small.

Now sulphur is a very strongly electronegative element, and presumably a sulphur molecule would be very likely to capture an electron striking against it. Thus a slight amount of sulphur vapour would result in a great diminution in the life of an ion, and therefore of its power, as an ioniser. That there is sulphur vapour produced when the discharge is going is proved by the fact that there is a visible deposit of sulphur on the walls of the tube after the discharge has been going for some time.

The effect produced by electronegative elements can be explained by the effect they produce on the life of the electron, but the electronegative elements are not the only ones which retard the discharge. Effects of the same type, though not so pronounced, are produced, for example, by certain metals, and the preceding explanation would not apply to them. It would seem as if these produced the effect, not by removing the electrons—the ionising agent—but by removing from the gas something which is more easily ionised than the normal molecule. The discharge, when it passes through the gas, besides producing chemical combinations and decompositions, may produce other modifications of the gas which only last for a short time, but which are more easily ionised than the normal molecules. In many gases—oxygen and nitrogen are conspicuous examples—the existence of such modifications is shown by bright after-glows which may persist for several seconds after the discharge has stopped. In other gases, where the duration of these modification is too short for them to show visible after-glows, their existence may be inferred from the changes which occur in the properties of the gas through which the discharge has passed. The discharge shows very marked hysteresis. If we

begin with a very small spark-gap between the terminals of the induction coil and increase its length until the ring discharge begins to pass through the gas, this length will be longer than that at which the ring discharge will disappear if we start with a very long spark-gap and gradually diminish it until the discharge stops. It does not require so large an electromotive force round the circuit to maintain the discharge as it does to start it. The simplest explanation of this is that the discharge produces systems which are more easily ionised than the normal molecule. These systems may either be aggregates formed by the molecules, or they may be molecules in an "excited" state, like those by which we explained the action of light on the discharge. When the molecules are in the "excited" state they are more active chemically than the normal molecules, and they will thus tend to combine with substances present in the discharge tube. If, then, any substance which has a strong affinity for these easily ionised molecules is present in the discharge tube, it will remove them from the gas as fast as they are formed, and thus make the passage of the ring discharge more difficult. Evidence of the effect of certain metals on systems formed in the gas by the discharge is afforded by experiments on the after-glows to which we have already alluded; the presence of these metals in the discharge tube completely stops the after-glow in gases which in their absence give intense glows. The metals destroy the systems which produce the glows. These systems are probably analogous to the easily ionised ones which assist the discharge; if the metals destroy these, their presence will make the discharge more difficult.

Chemical Combination Produced by the Ring Discharge.

A property of the electrodeless discharge which may, I think, have important applications to chemistry, is that of giving to the gas through which it passes very active chemical properties, and causing it to enter into chemical combinations and produce compounds, some of which are unexpected. The discharge puts some of the atoms and molecules of the gas into the "excited" state, and when in this state their chemical activity is enhanced. One reason for this is that their electrostatic moment is increased, and they are therefore more likely to combine with other systems than when they are in the normal state. I shall this afternoon confine myself to a few cases where the combination is between the gas through which the discharge is passing and solids placed in the tube. This combination may be detected by measuring the changes of pressure due to the passage of the discharge; the chemical combination will produce a diminution in pressure. In some cases this diminution is so rapid that the pressure falls below the value at which the discharge will pass, and to maintain the discharge a stream of gas must be kept flowing through the tube. It is necessary when investigating the combination between the gas and a solid to measure the changes of pressure both before and after the introduction of the solid into the tube, for in some cases—hydrogen especially—there is often a considerable diminution of pressure even without the introduction of other bodies into the tube. The first case I shall consider is that of the formation of oxides of magnesium higher than MgO. The ring discharge through oxygen at certain pressures produces a brilliant phosphorescence in any MgO inside the tube. When experimenting with this I found that the pressure of the oxygen fell so rapidly that the discharge stopped after a minute or two. On measuring the pressure it was found to have fallen to less than 0·01 mm. On introducing fresh oxygen the process

was repeated, and a volume of gas which at atmospheric pressure would be many times the volume of the MgO in the tube was absorbed without any sign of the process coming to an end. The substance in the tube remained white, but it was evident that it was not the original substance, because it no longer showed the brilliant phosphorescence characteristic of MgO. The experiment was repeated many times with the same result, and no change of pressure in the oxygen occurred unless the MgO was in the tube. This I think showed that oxygen through which the ring discharge is passing combines with MgO to form a higher oxide. I understand that a higher oxide of magnesium is manufactured in considerable quantities, though it is not mentioned in the majority of text books on chemistry.

I found by the same method that oxygen through which the ring discharge is passing combines with CaO, and also with ZnO, to form higher oxides, though the rate of formation is not so rapid as for MgO.

I made an experiment to see if the thermionic emission from the higher oxide of calcium differed from that from CaO. Specks of the two oxides were placed close together on a platinum wire which was heated to incandescence by an electric current. The stream of electrons from the higher oxide was, I thought, visible at a slightly lower temperature than that from the CaO, but there was not a great deal of difference. Another reaction which goes on with great rapidity under the ring discharge is the combination of arsenic with hydrogen.

This chemical effect of the discharge is very intimately connected with the action of " getters " in producing high vacua. One " getter " which is much employed is phosphorus, and the rapidity with which the pressure falls when the ring discharge passes through nitrogen in the presence of phosphorus is very remarkable. It was so large that I thought it worth while to see if there would be any reduction of pressure if helium were substituted for nitrogen ; the pressure of the helium showed, however, no alteration.

I think that the study of chemical reactions produced by the electrodeless discharge is a promising field of investigation, and may throw light on the mechanism of some reactions and the discovery of new compounds.

XIV.—SOME ACOUSTICAL PHENOMENA ILLUSTRATED BY RIPPLES—TRANSMISSION THROUGH QUINCKE FILTERS, CURVED CONDUITS AND VIBRATING PARTITIONS.

By A. H. Davis, *D.Sc.*, Physics Department, The National Physical Laboratory.

Abstract.

The Paper employs ripple photographs to illustrate the action of the Quincke acoustical filter, and draws attention to the filtering action which is likely to occur at bends in curved sound conduits or in curved horns owing to resonant transverse vibration of the contained air. It also illustrates by the ripple analogy the transmission of sound through partitions, showing how the characteristics of the transmission may vary as the natural frequency of the partition is raised.

IN a previous Paper,* in which the analogy between ripples and acoustical phenomena was established, some examples were given of ripple analogues to acoustical conditions. The present Paper gives further illustrations of some interest.

I. Conduit with Quincke Filter.

Photographs have been taken illustrating wave transmission through a straight conduit fitted with a model acoustical filter of the type due to Quincke. A Quincke filter consists of a resonator or a stopped pipe of adjustable length fixed to the side of a sound conduit. It prevents waves of certain definite frequencies from passing along the conduit. The frequencies suppressed are those natural to the resonator, so that a stopped pipe of (corrected) length l acts as a filter to waves of length λ if $l=\lambda/4$, $3\lambda/4$, $5\lambda/4$, etc.

In photographing ripple transmission through narrow conduits by the method of the earlier Paper, any water meniscus at the boundary of the conduit gives optical distortion of the wave image on the screen. On this account a special technique was developed for the work. The boundaries of the conduit and of the filter were constructed of teak of 2 cm. thickness, and were firmly cemented in proper relative position on a sheet of plate glass. The upper surface was planed carefully to ensure that an accurately level upper surface was obtained. The model thus assembled was then laid on levelling wedges in the ripple tank, and was adjusted to be level, and thus parallel with the surface of the water. The depth of water in the tank was adjusted so that the surface of the wood was barely emergent. With this adjustment, the meniscus effect was eliminated when the water was undisturbed, but occurred to some extent as the trough of the wave passed along the conduit.

Photographs of wave transmission through the conduit were then taken for different adjustments of the length of the Quincke filter tube at the side. The frequency of the ripples, about 8 cycles per second, was the lowest at which good waves were obtained with the apparatus used. For lower frequencies the main waves were accompanied by small subsidiary wavelets, which apparently travelled

* Proc. Phys. Soc., Vol. 38, p. 234 (1926).

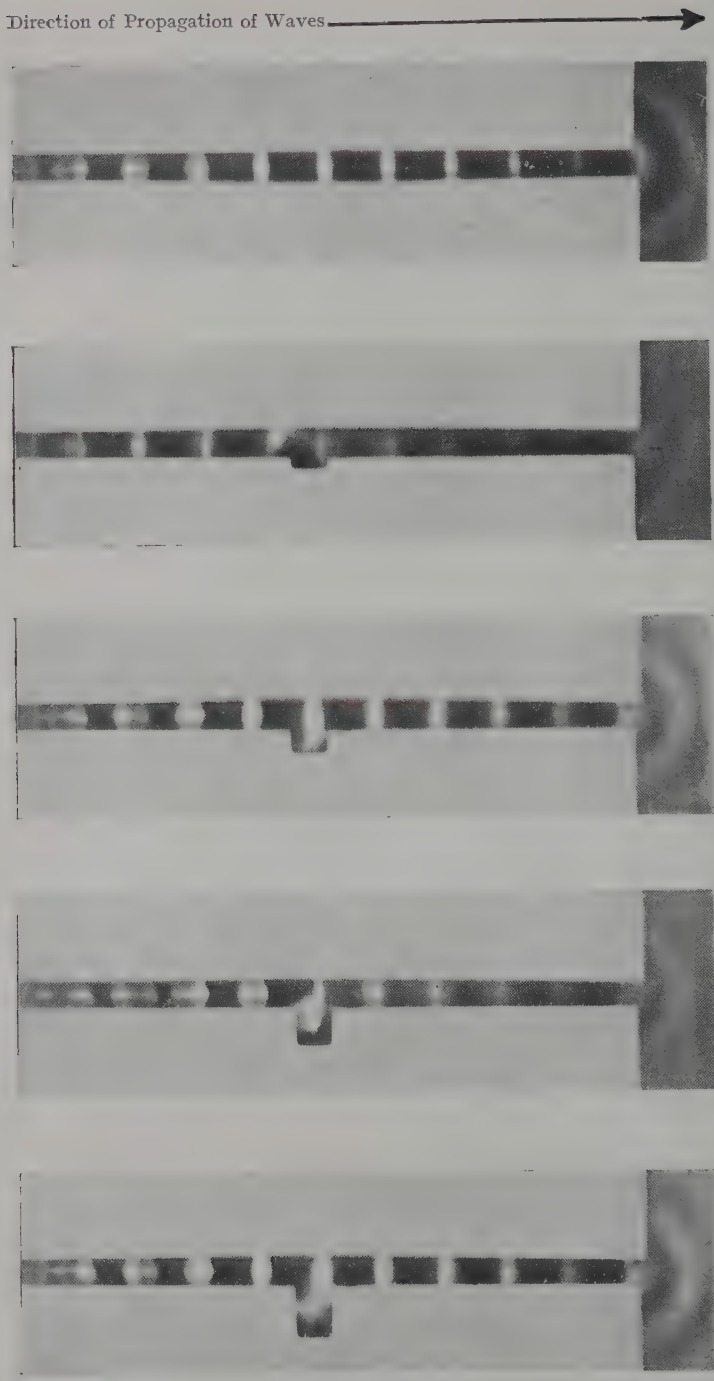

Direction of Propagation of Waves
No Filter.
First Resonance (Filter effect observed).
Intermediate (No Filter effect).
Second Resonance (Filter effect observed).
Beyond Second Resonance (No Filter effect).

FIG. 1.—QUINCKE FILTER EFFECTS.

[*To face page* 91

slowly and dropped back into the main waves after about 4 wavelengths had been traversed. To obtain a clear outline of the conduit, a second photograph of the boundary was taken in each case by stopping the wave generator and increasing the depth of water in the tank slightly, so that the model was completely immersed. For printing purposes a negative of the wave photograph was superimposed upon a glass positive of the outline, and prints were obtained by printing in parallel light through the two plates when accurately registered.

The results are shown in Fig. 1. The various photographs show wave transmission through a conduit in the absence of the filter, the success of a Quincke filter when tuned to resonance directly or harmonically, and the absence of filtering when the filter is mistuned.

II. Curved Conduit.

During some experiments with a curved conduit representing a section of a loud-speaker horn, it was noticed that pronounced stationary waves occurred at a certain bend, the direction of vibration being transverse to the axis of the horn. For frequencies at which such transverse resonance occurred, waves were largely suppressed in transmission through the conduit, little energy emerging from the flare. The bend was, in fact, acting as a wave filter, owing to the dissipation of wave energy in transverse vibration. The filter effect was observable over a moderate band of frequency, but when the frequency of the waves was markedly altered the transverse stationary undulation broke down, and waves emerged freely from the flare of the horn.

The scale of the experiment was such that the resonant frequency observed would correspond to a frequency of 5400 cycles per second if the horn were a moderately large one with a flare of $2\frac{1}{2}$ feet wide. The suppression of this particular frequency would not be of great importance as far as the reproduction of speech or music were concerned. It was not practicable at the time to try lower frequencies; but, on the above scale, the conduit at the bend had a width corresponding to 7 inches, for which lowest mode of transverse stationary undulation should occur with a frequency of about 900 cycles per second, well within the important range of hearing.

In connection, therefore, with curved or folded horns, the tendency for transverse vibrations of the air to be set up at bends must not be overlooked. The effects in the acoustical case, however, would not necessarily be so pronounced as in the ripple experiment, unless there were the possibility of corresponding dissipation of energy at the bend.

As regards other forms of conduit, it is interesting in this connection that, in testing voice tubes in 90° bends of 10-foot length, Eckhardt, Chrisler and Quayle* found their largest tube, which was 4 inches in diameter, transmitted a lower percentage of sound for frequencies in the region of 2000 cycles per second than for those in the regions of 1000 and of 3000 cycles. They comment on this, but are unable to offer an explanation. Now, according to the formula in Lamb's "Sound," 2nd ed., p. 263, 1926, the lowest frequency of radial vibrations of the air contained in a 4" cylindrical tube is about 1950 cycles per second, and it seems possible that the low transmission they found in this region may have been due

* Bur. Stds. Tech. Papers 21, No. 333, p. 162 (1926).

to the filtering effect arising from radial resonance. Consistently with this view transmission through the 2-inch tube fell off at higher frequencies, and it may be that it was the 3-inch tube, which showed no falling off, which was exceptional.

III. Wave Transmission Through a Partition.

In a certain method of measuring transmission of sound through building partitions, a test partition covers an aperture in a sound-proof wall between two adjacent rooms. On one side a more or less parallel beam of sound is incident obliquely upon the partition, and on the other measurements of sound intensity are made along the continuation of the axis of the incident beam.

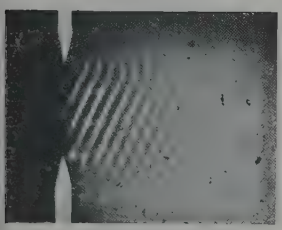
Now it may be shown by calculation that sound is transmitted by partitions mainly through vibration of the partition, and not by wave transmission from particle to particle in the wall. It might then be expected that vibration of the partition would result in sound being sent out at right angles to the partition rather than in the oblique direction of the incident beam, particularly if the stiffness of the partition were a predominant factor. But it must be remembered that the fundamental natural frequency of building partitions is usually very low compared with the frequency of ordinary sounds, and it is mass, and not stiffness, which is the dominant factor. In actual practice the author has frequently observed by ear that a beam of sound incident obliquely upon a partition emerges as an oblique beam from the other side, and measurements with light partitions, in collaboration with Mr. T. S. Littler, M.Sc., contribute substantially to this general observation.

In this connection, therefore, the ripple photographs of Fig. 2 were taken some time ago as a preliminary test of the validity of a beam method for transmission tests of partitions. The first photograph shows a parallel beam of ripples incident upon the left-hand side of an aperture in a solid wall dividing the ripple tank into two parts; transmission of the oblique beam through the aperture is observed. The distance of the observing screen from the tank was chosen to give good definition for the transmitted waves, and the blurring of the incident waves arises from this choice rather than from any imperfections of the waves themselves.

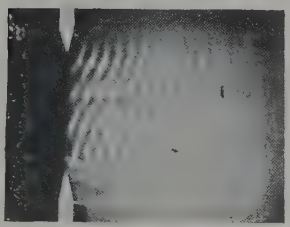
The position of the aperture has been clearly marked on the photographs in white, and the pointed ends shown are in reality the plans of two small vertical vices, in which a rubber membrane could be so clamped that the lower half was in water and the upper half in air. In the second photograph a thin rubber membrane covers this aperture, but is quite slack. Transmission is now less pronounced than when the aperture is uncovered, but the oblique beam is preserved. In the next photograph the membrane has been appreciably stretched—evidenced by an increased gap width—and is approaching the condition of resonant vibration of the membrane. There is now evidence of transmission normal to the membrane as well as in the direction of the incident beam. Slightly greater stretching resulted in the fourth photograph of the series, in which the emergent beam is mainly normal to the membrane, presumably owing to resonant vibration. Stretching beyond this point resulted, as in the fifth photograph, in a return to more complicated conditions. Stretching the membrane so tightly that the aperture points lay outside the limits of the photograph resulted again in the emergence of waves normal to the membrane. This completes the series of photographs obtained.

It should be stated that the photograph with the slack membrane was easily

Membrane Absent.

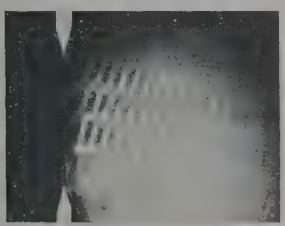


Membrane Slack.



Approaching Resonance.

Resonance.



Beyond Resonance.

Membrane Tightly Stretched.

FIG. 2.—PHOTOGRAPHS SHOWING VARIATION IN WAVE TRANSMISSION THROUGH A MEMBRANOUS PARTITION AS THE NATURAL FREQUENCY OF THE MEMBRANE IS RAISED BY INCREASING ITS TENSION.

To face page 92]

obtained in the first instance, but was more difficult to repeat. The rubber membrane was very thin indeed, and, after it had been in position and thus partially immersed in the water for some time, the upper part of the membrane which emerged from the water tended to be drawn down upon the surface by meniscus forces. With the membrane slack this was troublesome, and the membrane had to be supported above the water at a number of points by means of a fine thread. Presumably, this "leaning over" of the upper part of a slack membrane stiffened its resistance to the progress of waves.

I am indebted to Mr. R. Berry, Observer in the Physics Department, for assistance with the experiments and photographs.

DISCUSSION.

Major W. S. TUCKER said that the author had shown a mastery of the difficult technique of the ripple tank. He was particularly interested in Section II of the Paper, which dealt with transverse resonance occurring at an elbow bend in a loud-speaker horn. In listening trumpets much distortion is experienced owing to the fact that the polar curve of reception of such a trumpet is a function of the frequency. Even when the source of sound is on the axis of the trumpet some distortion occurs, and this rapidly increases as the direction of the sound becomes more oblique. It is on this account desirable to turn the horn towards the source; but, apparently, when this is done another cause of distortion is introduced in the transverse resonance described by the author. The author's work on partitions seemed to indicate that resonant walls may become secondary radiators of sound; this fact must be taken into account in designing the walls of an aeroplane cabin.

Dr. A. B. WOOD referred to the author's remark that the natural frequency of building partitions is usually low. If the frequency were 100, for instance, the corresponding wave-length would be 10 ft., which was large compared with the size of a door. The author's diaphragms (Fig. 2) appeared, on the other hand, to be large compared with the wave-length. Were his inferences valid in view of this disparity?

Dr. E. T. PARIS (communicated): I would like to express my appreciation of the very interesting photographs taken by Dr. Davis which appear to me to illustrate in a very clear manner the different acoustical phenomena mentioned in his Paper. In connection with the photographs illustrating the action of a Quincke filter, I would like to ask whether the width of the resonator has any influence on the amplitude of the transmitted ripple. The reason for asking this question is that the photographs seem to show that, even when there is no filter, there is a perceptible dying away of the ripples as they pass along the main conduit. In the corresponding acoustical case it is generally assumed that there is no dissipation of acoustical energy either in the main conduit or in the resonator, and in these circumstances there should, theoretically, be complete reflection of the incident sound-waves at the resonator when the length of the latter is one-quarter of a wave-length. Also this effect is independent of the relative diameters of the main conduit and the resonator. If, however, there is attenuation of the sound-waves it is not obvious that the same result will hold good. In fact, from a rough calculation, it appears likely that the filtering effect depends to some extent on the diameter as well as the length of the resonator. I would therefore like to know whether, in Dr. Davis's experiments, anything has come out that would indicate that the width of the resonator has any influence on the filtering effect. I would also like to suggest to Dr. Davis an experiment with the ripple-tank which I think would be of interest. The experiment I have in mind is one to illustrate the reflection of sound from a porous surface, and in particular the conditions under which the reflected wave may vanish. If plane waves are incident on a plane reflecting surface in which there is a number of long narrow pores—so long and so narrow that any sound which enters them is stifled (owing to viscosity) before it reaches the ends of the pores—then there is always some angle of incidence for which the reflected wave should vanish. That is, there is complete absorption of the sound for that angle of incidence. According to the theory given by Rayleigh, the cosine of the angle of incidence for total absorption is equal to the area occupied by the pore-openings per unit area of reflecting surface. This phenomenon would be a difficult one to show with sound-waves, but it seems that it could be readily illustrated with the ripple-tank apparatus which Dr. Davis has at his disposal. All that would be required is a

straight barrier to reflect the ripples, with a number of canals leading off at right angles. If different angles of incidence were tried, one should be found at which there is no reflected wave. I think the experiment, if it can be performed, would be of considerable interest.

Author's reply: In reply to Dr. Wood, the scale of the ripples in Fig. 2 is suitable for showing the phenomena which may occur in transmission of sound through building partitions. The wave-length of the ripples (1·4 cm.) relative to the size of the aperture (about 14 cm.) corresponds to a sound of frequency of 450 cycles per second incident upon a 25 ft. partition, or to one of about 2000 cycles incident upon a 6 ft. partition. In the earlier photographs the natural frequency of the partition is much lower than the ripple frequency; a condition which corresponds, within the limits of the analogy, to the case in actual practice where the gravest mode of building partitions (say 100 per second or much lower) lies well below the frequency of the majority of incident sounds. The beam of ripples in these conditions is seen to pass straight through—a confirmation of my experience that an obliquely incident beam of sound passes through a building partition without change of direction. The later photographs show how different things would be if the partition had an important natural frequency in the region of the frequency of the incident sound. In reply to Dr. Paris, there is relatively greater dissipation of energy in a ripple conduit than in an acoustical one, and he is correct in his deduction that the width of the Quincke filter did influence the amplitude of the transmitted ripples. The width of resonator (2 cm.) shown in the photographs was the minimum with which a reasonable demonstration of the filter effect could be obtained with the conduit used. It will be a pleasure to try, on some convenient occasion, the experiment on wave reflection from an absorbent wall that Dr. Paris suggests. In response to suggestions by Mr. Albert Campbell and Capt. C. W. Hume, a short definition of the Quincke filter has been included in the Paper.

XV.—A SIMPLE GRAPHIC METHOD FOR THE DETERMINATION OF GALVANOMETER AND FLUXMETER CONSTANTS, WITH A NOTE ON THE MEASUREMENT OF INTENSE MAGNETIC FIELDS.

By Allan Ferguson, *M.A.*, *D.Sc.*, and Eric J. Irons, *B.Sc.*, East London College, E.1.

Received December 9, 1927.

Abstract.

This Paper deals with methods for evaluating the principal construction constants of moving coil instruments by the graphical treatment of observations of logarithmic decrement and its variation with circuit resistance. It also discusses the application of these methods to the measurement of intense magnetic fields.

Galvanometer.—General Theory.

THE behaviour of a galvanometer may be defined in terms of its operation constants*—that is, in terms of its period and of the half-dozen sensitivities which it possesses. These operation constants in turn depend on the intrinsic or construction constants of the instrument, and it is the principal object of this note to describe a simple graphic method for their determination. A secondary object is pædagogic in character. From the teacher's point of view a galvanometer illustrates admirably the dynamics of a vibrating system, and a little drill of the type to be described greatly assists students to comprehend the capabilities and limitations of the instruments which they may be called on to use. The galvanometer designer is interested in the magnitude of the construction constants and in their relation to the operation constants. The construction constants with which we are concerned are the moment of inertia (K) of the deflected system, the displacing couple per unit current† (Q), the open circuit damping coefficient (p_0), the restoring couple per unit displacement (μ), and the resistance (G) and self-inductance (L) of the galvanometer. The effects of self-induction are commonly omitted, and the method we are about to describe has the advantage of showing whether or not the omission is justifiable.

Writing the equation of motion of the coil in the form

$$Q\gamma - p_0\dot{\theta} - \mu\theta = K\ddot{\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where θ is measured in the usual way and γ is the current at any instant, we have, where N is the flux through the coil in its displaced position, and e is the external electromotive force acting on the circuit, whose *total* resistance is R.

$$N = Q \sin\theta - L\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1{\cdot}1)$$

$$\gamma = (e - \dot{N})/R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1{\cdot}2)$$

* Wenner, Bull. Bureau Stand. 13, No. 2 (1916).

† We restrict the discussion to underdamped moving-coil instruments with critical damping as a limit. Q is thus the "nAH" of elementary theory.

from (1), (1·1) and (1·2) we have, if the self-inductance is small.*

$$(K+LQ^2/R^2)\ddot{\theta}+(p_0+Q^2/R)\dot{\theta}+\mu\theta=Qe/R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If no external electromotive force is acting, (2) may be written

$$\ddot{\theta}+p\dot{\theta}+q\theta=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$p=(p_0+Q^2/R)\div(K+LQ^2/R^2),\ q=\mu\div(K+LQ^2/R^2) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

GALVANOMETER.—SELF-INDUCTANCE NEGLIGIBLE.

If we suppose that the self-inductance may be neglected we have at once for an underdamped system, remembering that $4n\lambda=p$,

$$4R(n\lambda-n_0\lambda_0)=Q^2/K, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where λ is the logarithmic decrement corresponding to a frequency n, and λ_0 and n_0 are the corresponding quantities on open circuit. It is not uncommon to assume that n is independent of λ, and keeps its open circuit value n_0, in which circumstances (5) becomes

$$Q^2=4KRn_0(\lambda-\lambda_0), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

an equation which gives the justification of the well-known rule that λ is a linear function of the reciprocal of R.

Keeping to the general case and remembering that $q=4n^2(\pi^2+\lambda^2)$ we have, substituting for n in (5),

$$2q^{\frac{1}{2}}\times R\lambda/\sqrt{(\pi^2+\lambda^2)}=4n_0\lambda_0R+Q^2/K, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and we see that a plot of $R\lambda/\sqrt{(\pi^2+\lambda^2)}$ as y against R as x gives a straight line whose slope and intercept determine Q^2/K and q(or μ/K). Whether L is negligible or not, we have on open circuit

$$4n_0\lambda_0=p_0/K\ ;\ 4n_0^2(\pi^2+\lambda_0^2)=\mu/K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which determines p_0/K and gives a check determination of μ/K. It remains to determine K, and this is done by taking periods and logarithmic decrements for the coil on open circuit, first unloaded (n_0, λ_0), second, when loaded (N_0, Λ_0) with a body of known moment of inertia K_1.† We then have, taking account of the fact that the loading may alter the damping coefficient p_0,

$$(K+K_1)/K=n_0^2(\pi^2+\lambda_0^2)/N_0^2(\pi^2+\Lambda_0^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

K being thus determined, the other intrinsic constants p_0, μ and Q follow at once from a knowledge of the variation of logarithmic decrement with total circuit resistance. It is of course assumed that G, the galvanometer resistance, has been independently determined.

* If this restriction be removed, the equation of motion becomes a linear third-order differential equation, the development of which, in a form not so convenient for our purpose, follows the lines laid down in Maxwell, "Elec. and Mag.," II, 405 seqq.

† A glass (not metal) rod is suitable.

An important operation constant is R_1, the total circuit resistance which just produces critical damping. This may be determined directly by noting the resistance for which the motion just ceases to be oscillatory, or by making use of the property that the time of return to the zero is a minimum when the damping is critical. Whichever of these methods is adopted, the value obtained for R_1 depends considerably on the judgment of the individual observer, and a more reliable value is that deduced from the experimentally determined intrinsic constants. This may be done by means of equation (3), which for critical damping gives

$$R_1=Q^2/(2\sqrt{\mu K}-p_0)=Q^2/K\div(2\sqrt{\mu}/\sqrt{K}-p_0/K) \quad . \quad . \quad . \quad . \quad (10)$$

all the quantities on the right-hand side of equation (10) being known. More neatly, we may read it off at once from the straight-line graph of equation (7). For when $R=R_1$ the logarithmic decrement becomes infinite, and $\lambda/\sqrt{(\pi^2+\lambda^2)}$ becomes unity. Hence the critical value of R is the abscissa of that point for which y is equal to x, or in terms of the slope (m) and the intercept (c) of the straight line

$$R_1=c/(1-m) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

It may be noted in passing that one of the disadvantages of the approximate equation (6) is that it cannot be used in this way to determine the critical resistance.

Galvanometer.—Self-Inductance Appreciable.

Should the graph of equation (7) show any pronounced curvature, it may be due to the fact that the self-inductance of the galvanometer coil is not negligible.

Proceeding as before, we still have

$$4n\lambda=p, \quad 4n^2(\pi^2+\lambda^2)=q,$$

where p and q now have the values given in (4).

Eliminating n we easily obtain

$$\frac{2\lambda}{\sqrt{(\pi^2+\lambda^2)}}\cdot\sqrt{\left(\frac{\mu}{K}\right)}\cdot\left(1+\frac{1}{2}\frac{LQ^2}{KR^2}\right)=4n_0\lambda_0+\frac{Q^2}{RK} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Treating μ/K as known from equation (8) we may put

$$\frac{2\lambda}{\sqrt{(\pi^2+\lambda^2)}}\cdot\sqrt{\left(\frac{\mu}{K}\right)}-4n_0\lambda_0=Y, \text{ and } \frac{2\lambda}{\sqrt{(\pi^2+\lambda^2)}}\sqrt{\left(\frac{\mu}{K}\right)}=X,$$

and we have

$$RY=-\frac{1}{2}\frac{LQ^2}{K}\cdot\frac{X}{R}+\frac{Q^2}{K} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The test of the negligibility of L is therefore the constancy of the product RY. If this product shows signs of systematic variation, a plot of RY against X/R will determine a straight line from the slope and intercept of which both L and Q^2/K may be deduced.

FLUXMETER.—SELF-INDUCTANCE AND TORSIONAL CONTROL NEGLIGIBLE.

The simple theory of the fluxmeter gives us, for an impulsive couple,

$$\frac{Q}{R}\int e\,.\,dt=\frac{QF}{R}=K\omega_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where ω_0 is the initial angular velocity and F the flux cut. The equation of motion of the coil being

$$\ddot{\theta}+p\,\dot{\theta}+q\theta=0$$

we obtain at once, if q be negligible and α be the amplitude of the throw,

$$p\alpha=\omega_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

or
$$(p_0+Q^2/R)\alpha=K\omega_0=QF/R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Writing this in the form

$$R\alpha=-Q^2\alpha/p_0+QF/p_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

we see that if we vary the total circuit resistance and employ a constant known flux F, a plot of $R\alpha$ as y against α as x determines the constants Q and p_0.

FLUXMETER.—SELF-INDUCTANCE APPRECIABLE, TORSIONAL CONTROL NEGLIGIBLE.

The equation of motion is still

$$\ddot{\theta}+p\dot{\theta}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where p is now given by

$$p=(p_0+Q^2/R)\div(K+LQ^2/R^2).$$

Substituting in (17) we obtain on reduction

$$p_0R\alpha+Q^2\alpha=QF+LQ^3F/KR^2.$$

This is a four-term equation, but we can reduce it to a three-term form by taking the origin at some *known* point $(R_0,\ \alpha_0)$ on the curve between R and α considered as variables, F being constant. This gives us

$$p_0(R\alpha-R_0\alpha_0)=Q^2(\alpha_0-\alpha)+LFQ^3/K\,.\left(\frac{1}{R^2}-\frac{1}{R_0^2}\right) \quad . \quad . \quad . \quad . \quad . \quad (21)$$

which, divided throughout by $(\alpha_0-\alpha)$, obviously gives a rectilinear graph.

FLUXMETER.—TORSIONAL CONTROL APPRECIABLE, SELF-INDUCTANCE NEGLIGIBLE.

If we take the equation of motion as

$$\theta+p\dot{\theta}+q\theta=0$$

retaining the q term, which is *ex hypothesi* small, so that the system is heavily over-damped, we may write the solution as

$$\theta=exp.\ (-pt/2)[A\ exp.\ \sqrt{(p^2/4-q)}\,.\,t+B\ exp.\ -\sqrt{(p^2/4-q)}\,.\,t]$$

Introducing the conditions that when $t=0$, $\theta=0$ and $\dot{\theta}=\omega_0$, and that when $\theta=\alpha$, $\dot{\theta}=0$, we readily find that

$$q\alpha^2=\omega_0{}^2\left[\frac{p/2-\sqrt{(p^2/4-q)}}{p/2+\sqrt{(p^2/4-q)}}\right]^{p/2\sqrt{(p^2/4-q)}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

which, remembering that q is small in comparison with $p^2/4$, may be written

$$(p^2-q)\alpha^2=\omega_0^2\left(\frac{q}{p^2-q}\right)^{2q/p^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

This reduces, as it should, to (17) when q is negligible.

We see that for a constant circuit resistance ω_0 and therefore F remains proportional to α, but the constants are considerably more difficult to determine.

Measurement of Intense Magnetic Fields.

A knowledge of Q ($\equiv nAH$) obviously affords a means for determining H, the field in which the coil swings, if the effective area of the coil be known. This method has been used by Klopsteg,* who, however, was content to work with the approximate equation (6). This restriction seems to be quite unnecessary, as the more exact equation (7) is just as easy to handle, and involves no restriction of the range over which logarithmic decrements may be taken. Klopsteg determines his moment of inertia directly. This is fairly easily done with a special coil, but in the handling of galvanometer coils occasions arise when a direct determination of K is not easy. In these circumstances it is much more convenient to determine Q by making a direct determination of the current sensitivity (S_c) or the voltage sensitivity (S_e) in a circuit of total resistance R. By putting $\ddot{\theta}=\dot{\theta}=0$ in equation (2) we see that

$$Se=Q/\mu R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Let us now write this in terms of the slope (m) and of the intercept (c) of the rectilinear graph of equation (7). We then have

$$Q=\frac{mc}{Rn_0\lambda_0 S_e}=\frac{mc}{n_0\lambda_0 S_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

This method of determining Q provides a very simple means for measuring strong magnetic fields, given a coil of known effective area. The necessary operations are quite straightforward, comprising as they do a measurement of sensitivity and of logarithmic decrement of the system for various external resistances.

Measurements.

We proceed now to give the details of measurements made on certain moving-coil instruments.

Galvanometer A.—(Maker's stamp absent. Ordinary rectangular coil galvanometer.)

$R\times10^{-2}$:	5	7	10	20	30	40	50	60	80	100
$\lambda\times10^2$:	53·02	38·22	27·83	15·77	11·59	9·61	8·37	7·65	6·60	6·01
RY† :	112·0	110·6	111·0	112·0	110·4	110·9	110·1	112·1	111·0	111·8

Resistance (G) of galvanometer=29·4 ohms.

$$T_0=8''\cdot70\,; \quad \lambda_0=0\cdot0358$$

Moment of inertia of vibrator employed (K_1)=1·874 gm.cm.^{2}

$$N_0=1/14\cdot37\,; \quad \wedge_0=0\cdot09613.$$

* Physical Review, 2, 390 (1913).
† Vide equation (15).

From equation (8)

$$\frac{K+K_1}{K}=\frac{n_0^2}{N_0^2}\cdot\frac{\pi^2+\lambda_0^2}{\pi^2+\wedge_0^2}=\left(\frac{14{\cdot}37}{8{\cdot}70}\right)^2\left(\frac{9{\cdot}871}{9{\cdot}966}\right)=2{\cdot}701$$

Hence $K=1{\cdot}102$ gm.cm.^{2}

$$\mu/K=4n_0^2(\pi^2+\lambda_0^2)=0{\cdot}5217 \text{ sec.}^{-2}$$

From graph (*see* Fig. 1)

$$\text{Intercept} \quad =76{\cdot}9=\frac{Q^2}{K\,.\,2\sqrt{q}}$$

$$\text{Slope} \quad =114\times10^{-4}=2n_0\lambda_0/\sqrt{q}$$

Hence $q=\mu/K=0{\cdot}5214$ (alternative value),

and* $\quad Q^2/K \quad =76{\cdot}9\times2\times\sqrt{(0{\cdot}5214)}=111{\cdot}0.$

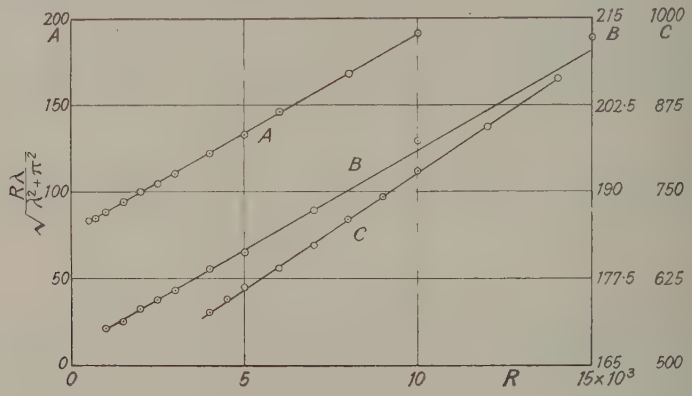


FIG. 1.

Hence for the constants of galvanometer *A*,

$Q=\sqrt{(111{\cdot}0\times1{\cdot}102)}=11{\cdot}06$ (arbitrary units)

$\mu=0{\cdot}5216\times1{\cdot}102=0{\cdot}5748$ gm.cm.^{2} sec.$^{-2}$

$p_0=4n_0\lambda_0K=0{\cdot}01814$ gm.cm.^{2} sec.$^{-1}$

$K=1{\cdot}102$ gm.cm.^{2}

$R_1=c/(1-m)=76{\cdot}9(1+0{\cdot}01)=77{\cdot}7$ ohms.

Galvanometer C, by Nalder Bros. & Co., Westminster, No. 26806. (The coil is wound in two parts which for our purposes were connected in series.)

$R\times10^{-2}$:	40	45	50	60	70	80	90	100	120	140
$\lambda\times10^2$:	45·75	41·95	38·78	33·71	30·35	28·00	25·97	24·58	22·15	20·54
RY :	1132	1138	1139	1122	1119	1129	1121	1134	1124	1128

* Q^2/K is expressed in arbitrary units. The resistances concerned are measured in ohms.

Resistance (G) of galvanometer=217 ohms.

$$T_0=4''\cdot90\,;\quad \lambda_0=0\cdot10637$$

Moment of inertia of vibrator employed (K_1)=2·086 gm.cm.^{2}

$$N_0=1/5''\cdot88\,;\quad \wedge_0=0\cdot0999$$

From equation (8)

$$\frac{K+K_1}{K}=\frac{n_0^2}{N_0^2}\cdot\frac{\pi^2+\lambda_0^2}{\pi^2+\wedge_0^2}=\left(\frac{5\cdot88}{4\cdot90}\right)^2\left(\frac{9\cdot881}{9\cdot880}\right)=1\cdot440$$

Hence $K=4\cdot742$ gm.cm.^{2}

$$\mu/K=4n_0^2(\pi^2+\lambda_0^2)=1\cdot646 \text{ sec.}^{-2}$$

From graph (*see* Fig. 1)

$$\text{Intercept}=440\cdot6=\frac{Q^2}{K\,.\,2\sqrt{q}}$$

$$\text{Slope}\quad=3375\times10^{-5}=2n_0\lambda_0/\sqrt{q}$$

Hence $q=\mu/K=1\cdot656$ (alternative value),

and $Q^2/K\ =440\cdot6\times2\times\sqrt{(1\cdot656)}=1134$

Hence for the constants of galvanometer B,

$$Q=\sqrt{(1134\times4\cdot742)}=73\cdot33 \text{ (arbitrary units)}$$

$$\mu=1\cdot656\times4\cdot742=7\cdot830 \text{ gm.cm.}^2 \text{ sec.}^{-2}$$

$$p_0=4n_0\lambda_0K=0\cdot4116 \text{ gm.cm.}^2 \text{ sec.}^{-1}$$

$$K=4\cdot742 \text{ gm.cm.}^2$$

$$R_1=c/(1-m)=440\cdot6(1+0\cdot03)=454 \text{ ohms.}$$

Galvanometer B, by Crompton & Co. (This galvanometer has a circular coil and is fitted with a gold bifilar suspension.)

$R\times10^{-2}$:	10	15	20	25	30	40	50	70	100	150
$\lambda\times10^2$:	54·30	36·14	27·29	21·98	18·44	14·07	11·40	8·405	6·206	4·444
RY :	397·0	396·2	396·6	396·5	396·3	396·4	395·6	396·0	399·6	400·4

Resistance (G) of galvanometer=92 ohms.

$$T_0=5''\cdot30\,;\quad \lambda_0=0\cdot009095$$

Moment of inertia of circular coil=1·851 gm.cm.^{2} (calculated from its mass and dimensions)

$$\mu/K=4n_0^2(\pi^2+\lambda_0^2)=1\cdot406 \text{ sec.}^{-2}$$

From graph (*see* Fig. 1)

$$\text{Intercept} = 167{\cdot}3 = \frac{Q^2}{K \,.\, 2\sqrt{q}}$$

$$\text{Slope} = 0{\cdot}00288 = 2n_0\lambda_0/\sqrt{q}$$

Hence $q = \mu/K = 1{\cdot}420$ (alternative value),

and $Q^2/K = 167{\cdot}3 \times 2 \times \sqrt{(1{\cdot}420)} = 398{\cdot}7$

Hence for the constants of galvanometer C,

$Q = \sqrt{(398{\cdot}7 \times 1{\cdot}851)} = 27{\cdot}17$ (arbitrary units)

$\mu = 1{\cdot}413 \times 1{\cdot}851 = 2{\cdot}615$ gm.cm.^{2} sec.^{2}

$p_0 = 4n_0\lambda_0 K = 0{\cdot}01271$ gm.cm.^{2} sec.$^{-1}$

$K = 1{\cdot}851$ gm.cm.^{2}

$R_1 = c/(1-m) = 167{\cdot}3(1+{\cdot}003) = 167{\cdot}8$ ohms.

Fluxmeters.

Fluxmeters are rather more difficult to handle. The absence, or almost complete absence, of any torsional control brings forward much more prominently any small variation in other parts of the system. In particular, the experiments which we have made emphasise the importance of ensuring that the deflections of the instrument in opposite directions shall be equal, and that, in measuring the flux due to a change in a secondary circuit, deflections at make and break shall be sensibly equal—always assuming that the time constant of the primary has a reasonable value.

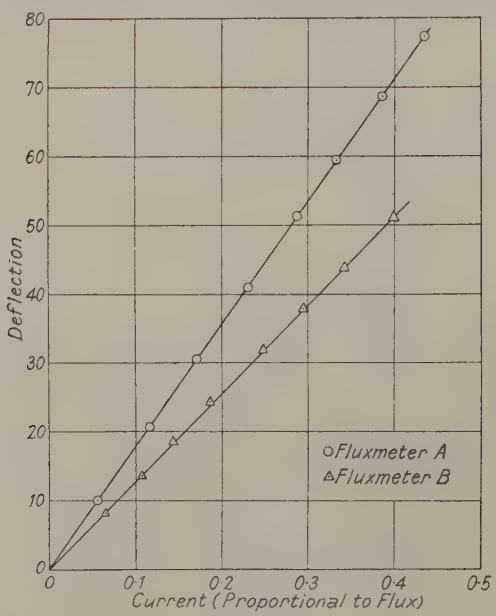


Fig. 2.

We feel that recent minor changes in fluxmeter design are retrograde in character. We refer specially to those instruments in which, in order to obtain a more open scale, the zero has been moved from the middle to one side of the scale. We would further emphasise the necessity for the careful examination of the regularity of the permanent field in which the coil swings.

In the experiments made two fluxmeters of different make were employed.

The fluxes used were not measured absolutely, as the flux was obtained from a short coil of inductance about 1 henry and resistance 16 ohms, on the outside of which was wound a secondary. The current in the primary was determined by measuring, on a Tinsley potentiometer, the P.D. at the ends of a standard resistance included in the circuit.

The extent of the throw in any one instance was measured from the position of rest taken up by the coil just before the secondary was made.

Two types of experiment were carried out—one in which the flux was varied and was taken as proportional to the current in the primary, the other in which the flux was kept constant, and the resistance in the fluxmeter circuit varied.

The graphs obtained are approximately in agreement with the formulæ given, but slight curvatures are in some instances shown. With one instrument, left and right and make and break swings are in fairly good agreement; with the other the differences are quite distinct.

Fluxmeter A (1 division=10,000 maxwells).

This instrument showed distinct differences between the readings to left and right, and smaller but appreciable differences between the readings at make and break. The mean readings, however, lay on a satisfactory straight line (*see* Fig. 2 *A*).

	Deflection.			Current.
	Left.	Right.	Mean.	(Proportional to flux.)
Make	9·9	10·4		
	9·9	10·4	10·1	0·056
Break	9·8	10·3		
Make	20·5	21·1		
	20·5	21·0	20·8	0·116
Break	20·5	20·9		
Make	30·3	31·1		
	30·3	31·0	30·6	0·171
Break	30·2	30·9		
Make	40·0	41·7		
	40·5	41·6	41·0	0·231
Break	40·9	41·5		
Make	50·3	52·3		
	50·3	52·4	51·3	0·288
Break	50·2	52·4		
Make	58·2	60·9		
	58·4	60·5	59·5	0·333
Break	58·6	60·1		
Make	67·0	70·3		
	67·3	70·2	68·7	0·386
Break	67·5	70·1		
Make	75·3	79·1		
	75·6	79·0	77·3	0·435
Break	75·9	78·9		

Fluxmeter B (1 division =14,000 maxwells).

With this instrument the readings left and right and at make and break were much more consistent. The plot of flux against deflection showed a slight but appreciable curvature (*see* Fig. 2 *B*).

	Deflection.			Current.
	Left.	Right.	Mean.	(Proportional to flux.)
Make	8·2	8·3		
	8·3	8·3	8·3	0·065
Break	8·3	8·3		
Make	13·6	13·6		
	13·6	13·7	13·6	0·107
Break	13·5	13·7		
Make	18·4	18·5		
	18·5	18·5	18·5	0·144
Break	18·5	18·5		
Make	24·3	24·5		
	24·3	24·5	24·4	0·189
Break	24·3	24·5		
Make	32·1	31·9		
	32·0	31·8	31·9	0·248
Break	31·8	31·7		
Make	38·0	38·0		
	38·0	37·9	37·9	0·295
Break	37·9	37·7		
Make	44·2	43·6		
	44·1	43·7	43·9	0·342
Break	44·0	43·7		
Make	51·2	51·0		
	51·3	51·1	51·2	0·400
Break	51·3	51·1		

This lack of linearity between flux and deflection was found to hold for the much smaller fluxes necessitating deflection measurements made by means of a lamp and scale.

With fluxmeter *B* the total resistance (*R*) in the fluxmeter circuit was varied and a plot of $1/\alpha$ against *R* was made for a constant flux. Here, again, anomalies were apparent, for while reciprocal deflections to the left or the mean reciprocal deflections plotted against *R* showed distinct curvature, reciprocal deflections to the right when plotted against *R* lay on a good straight line (Fig. 3).

Elementary fluxmeter theory assumes the *constancy of the field in which the coil swings* and the *absence of torsional control.*

If slight torsional control is present then, as we have seen, deflections remain proportional to flux in the absence of *any initial torsion.* The importance of these conditions in an instrument where controls are small, but not zero, has induced us to criticise the recent step taken in fluxmeter design of moving the zero to one end of the scale, thus preventing the user of the instrument from testing the equality of right and left deflections. Where discrepancies of four or five per cent. may be introduced, it is very advisable that means for checking these errors or for eliminating them may be provided.

Our thanks are due and are tendered to Prof. C. H. Lees for the interest he has taken in this work, and for the facilities which he has given for the carrying out

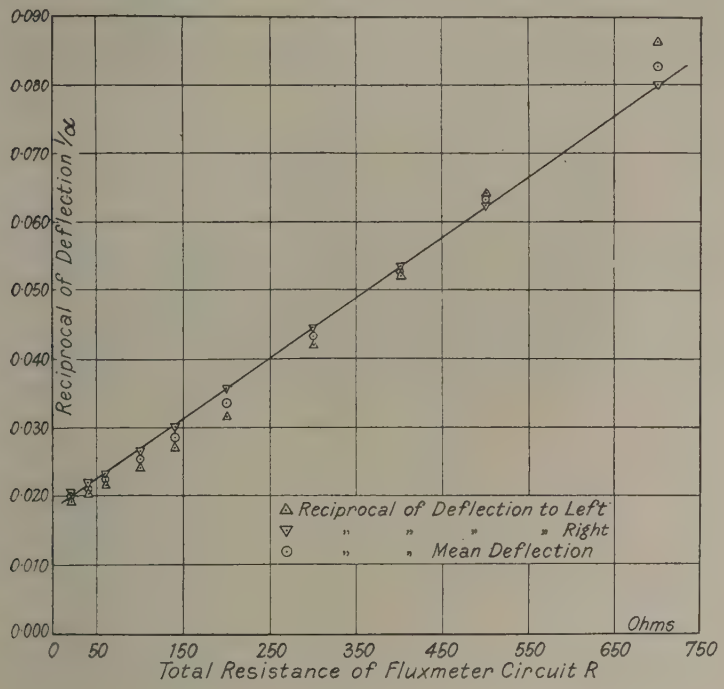


FIG. 3.

of the experiments; and to Prof. J. T. MacGregor-Morris our thanks are also offered for the loan of some of the instruments used.

DISCUSSION.

In presenting the Paper, Dr. FERGUSON suggested that instrument makers should revert to the practice of locating the zero at the centre of the fluxmeter scale, as the sensitivity in one direction often differs slightly from that in the other; and also that they should mark on instruments the values of constructional constants such as the number of turns in a coil and its area.

Dr. D. OWEN said that the Paper would be much appreciated by those making a study of the principles underlying the use of that important instrument, the moving-coil galvanometer. The assumption, however, of constancy of field for all positions of the coil was scarcely justifiable in an accurate treatment. It would thus be of interest to learn how far the values of constants as deduced by the methods of the Paper agreed with direct calculation, wherever this was possible. In regard to the fluxmeter, there could be no doubt of appreciable departure from constancy of field, and this fact involved a calibration of the scale for accurate work. It was much to be desired, on this and other grounds, that the fluxmeter should be provided with a means of zero

adjustment. He expressed the hope that the makers of these instruments would turn their attention to the remedy of what is a serious defect.

Dr. FERGUSON, in reply, said that if necessary it would be easy to insert in equation (1) a term in $dQ/d\theta$ to account for non-uniformity of the field, but the linearity of the graphs relating to galvanometers showed that this was unnecessary. In the case of fluxmeters the curvature of the graphs obtained indicated the presence of anomalies, but the curvature was definite and reproducible. The advantage of being able to read the throw in both directions was that this procedure indicated whether anomalies were present or not.

XVI.—THE APPLICATION OF ELECTRICAL RESISTANCE MEASUREMENTS TO THE STUDY OF THE ATMOSPHERIC CORROSION OF METALS.

By John Christopher Hudson.

Received October 20, 1927.

(*Communicated by* W. G. Bickley, M.Sc.)

Abstract.

This Paper describes in detail an experimental procedure for quantitative field tests on the atmospheric corrosion of metals, which is based on the determination of the change in the electrical resistance of wire specimens produced on exposure. The method is capable of great accuracy, and the resistance changes produced in duplicate specimens agree to within 5 per cent. The validity of the results has been established, in the case of the metals investigated, by correlation with the corresponding weight changes of the specimens. In the case of copper, it has been found that the percentage resistance change due to corrosion is inversely proportional to the diameter of the wire; it is thus possible to use the method as an "acceleration test" by conducting experiments on relatively thin wires, which are appreciably affected by corrosion within a few weeks.

CONTENTS.

I. Introduction.
II. Experimental Procedure:
- Brief description of the experimental methods.
- Method of fixing the terminals.
- Method of measurement.
- The experimental bridge.
- Methods of calculating and expressing the results.

III. Experimental Results:
- Short period corrosion tests on typical non-ferrous materials (Winter 1926-27).
- The effect of the length of the coil and of the gauge of the wire on the resistance changes produced by corrosion.
- Correlation of weight increment and resistance change (Stevenson screen exposure).
- Correlation of change in weight and resistance change for fully exposed specimens.

IV. Conclusion.
- Acknowledgments.

V. Appendix.
- Design and calibration of the stands used for outdoor exposure.

I. Introduction.

THE quantitative study of the corrosion of metals—by no means an easy task in the laboratory—becomes especially difficult when tests are to be made under actual service conditions. The difficulty is increased by the limited accuracy of the usual methods of measurement when applied to field tests, particularly in an investigation on atmospheric corrosion, where the rate of attack is, as a rule,

much less than in other cases of practical importance. Thus, a direct determination of the loss in weight of a specimen may be sufficiently accurate for practical purposes when a marked change occurs, as in the corrosion of iron by sea water. On the other hand, the losses in weight of non-ferrous materials on exposure to the atmosphere for a reasonable period are probably too small to render the results of very great value.* The first necessity, therefore, when the author was appointed in April, 1925, by the Atmospheric Corrosion Committee of the British Non-Ferrous Metals Research Association, to undertake systematic field tests on corrosion, was to devise much more accurate methods of measurement.

A method has been developed in which the increase in the resistance of a metallic conductor is taken as an index of its corrosion. The first observations of this type were made by Wilson,† who has followed the changes in the electrical and the mechanical properties of a number of aluminium alloys on exposure to the London atmosphere for a period of over twenty years. Although Wilson was not concerned with the use of the resistance determinations as a standard corrosion test, his results showed that measurable resistance changes were produced, and after two years' exposure the resistance of copper, aluminium and duralumin wires, $\frac{1}{8}$" in diameter, had increased by 2·0, 4·4 and 8·2 per cent. respectively.‡

The resistance method for studying corrosion is based on the fact that, as a result of corrosion, metal is removed from the specimen or replaced *in situ* by a non-conducting corrosion product.§ Consequently the effective conducting cross-section is diminished. Since the resulting percentage increase in the resistance of the specimen is equal to the percentage diminution in the cross-section, the method has the advantage of giving results that are immediately comparable for different materials. (The usual loss in weight test does not, unless the density of the metal is taken into account.) Apart from the accuracy with which the measurements can be made, the method has the further advantages that the tests can be conducted upon specimens of a convenient size, and that continuous observations may be made on the same specimen. These two assets are of especial value in the case of field tests.

It has been found that, if the tests are made on wires of a suitable diameter,

* The whole technique of gravimetric tests on atmospheric corrosion has been considerably improved by Vernon (Trans. Faraday Soc., 1924, 19, 839; 1927, 23, 113). In his weight increment method, the progress of corrosion is followed by determining the increase in weight of the specimens at convenient intervals. This procedure is particularly suitable for the study of the tarnish films developed in indoor atmospheres, and the accuracy obtainable is well demonstrated by the fact that he was able to follow the development of tarnish films on lead and aluminium in cases where the final weight increment, after 25 days' exposure, was as low as 0·28 milligrammes. The method can be used outdoors if the specimens are exposed in a Stevenson screen, but when the specimens are fully exposed the results are complicated owing to the removal of the corrosion product by the rain. Vernon (l.c.) overcame this difficulty by making simultaneous determinations of the metal removed in the rain water. Unfortunately, this procedure is too laborious to be applied on a large scale.

† E. Wilson, Proc. Phys. Soc., 39, 15 (1926); J. Inst. El. Eng., 63, 1, 108 (1925), and numerous other Papers.

‡ E. Wilson, B.A. Reports, p. 606 (1913).

§ The specific resistance of the corrosion product of the more common metals was determined by Bruhl (J. Inst. Met., 1911, 6, 279). The minimum value observed was about 1500 ohms/cm.^{3} for moist cuprous oxide; the figures for the dry products were much greater and ranged from 0·1 to 10 megohms/cm^3.

measurable changes in resistance are produced after a few weeks' exposure, which are accurately reproducible from one specimen to another. Moreover, the results obtained are in reasonably good agreement with the changes observed in other properties of the specimens, more particularly with their change in weight. The relation between these two quantities may be deduced as follows :—

The resistance of a wire of radius r is given by

$$R=k/r^2, \text{ where } k \text{ is a constant.}$$

By differentiation, $$100\,dR/R=-200\,dr/r.$$

The percentage increase in resistance ΔR, due to the corrosion of a thin uniform film of thickness dt on the surface of the specimen is thus

$$\Delta R=200\,dt/r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The weight of metal corroded $$W=A\,dt\,.\,D, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where A is the total area of the specimen and D the density of the metal.

From (1) and (2), $$dt=r\,.\,\Delta r/200=W/AD$$

Hence $$\Delta r=200\,W/A\,.\,D\,.\,r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or $$W=r\,.\,\Delta r\,.\,AD/200 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

By means of the last two equations the resistance change can be calculated from the loss in weight, and *vice versa*. The values so obtained are found to agree fairly well with the observed results; this fact supports the view that the resistance change is quantitatively proportional to the corrosion.

The experimental procedure for making corrosion tests by the electrical resistance method will now be described. It has already been successfully applied to most of the common non-ferrous metals, including copper, brass, bronze, nickel, nickel-silver, the copper-nickel alloys, nickel-chromium and aluminium.

II. Experimental Procedure.

Brief Description of the Experimental Method.

The tests are made on short lengths of wire wound into a coil of convenient size. In the earliest experiments the wires were 0·020 in. in diameter (24 S.W.G.); but, although the sensitiveness of the measurements is reduced by using thicker wires,* any irregularities due to pitting are correspondingly diminished, and it is therefore desirable to use the thickest wire that will give a measurable change. The gauge of the specimens has consequently been increased as this was warranted by the experimental results, and 18 S.W.G. wires (0·048 in.) have been used for the most recent work. This is approximately the gauge of a 40 lbs. to the mile telegraph wire.

* With the apparatus available, the sensitiveness is limited by the errors in the contact resistances, which are independent of the gauge of the wire. Since, however, the resistance of the specimen is inversely proportional to the cross-section (for a constant length of wire), and, as will be seen later, the change produced by corrosion varies inversely as the diameter, the experimental error is inversely proportional to the cube of the diameter, and the limiting thickness of wire is soon reached.

The wire is supplied by the manufacturers in the annealed condition, and as free as possible from surface defects. The specimens are made by winding the wire into coils $\frac{3}{4}$ in. in diameter, and cutting these up into lengths of 36 turns, or about 200 cms. of wire. Terminals of the same material are then attached to the ends of the wire by the method described later. The tests are usually made on sets of four duplicate specimens.

After a rinsing in acetone to remove any traces of grease the specimens are annealed.* The ends of the terminals are then amalgamated,† and the resistance of each of the four specimens is measured. After the resistance measurements, the amalgam is usually removed from the terminals by filing, although the presence of a little mercury at the end of the terminals does not seem to affect the corrosion of the coil itself.

Three of the specimens are then exposed in the atmosphere under investigation,‡ whilst the fourth is stored in the laboratory. The "blank" not only acts as a check on the constancy of the original resistances, but also compensates automatically for a number of possible experimental errors. At the end of the test, the resistance of the specimens is measured again, and the mean percentage change in the resistance of the exposed specimens, less any change that may occur in the "blank," is taken as proportional to the corrosion.

After this brief survey of the experimental procedure, it may be advisable to consider certain points in rather greater detail.

Method of Fixing the Terminals.

The resistance of the specimens is measured in an ordinary Wheatstone bridge circuit, and it is therefore necessary to minimise the contact resistances by fixing thick terminals to the end of the wire.§ Solder cannot be used for this purpose, because the juxtaposition of metal and solder might constitute a corrosion couple and cause abnormal corrosion by electrochemical action.

It was therefore necessary to devise a purely mechanical joint which could have no effect on the corrosion of the specimens. This difficult problem was finally solved by Mr. R. May, A.R.S.M., who suggested the method shown in Fig. 1. Blocks of the same material as the wire were milled out as shown in *A*, and the wire was inserted into a hole drilled in one end, which would just take it at a "push" fit. On hammering the block flat, an excellent joint was obtained (*B*).

* Usually in hydrogen at 250° for one hour, not including the time taken in heating up and cooling the furnace. This annealing is intended to remove any internal strain in the metal, and thus eliminate the possibility of "season cracking." This point has already been discussed elsewhere (Proc. Phys. Soc., 1926, 39, 24). The efficacy of low temperature annealing in preventing season cracking has been demonstrated by the work of Moore and his collaborators (J. Inst. Met., 1920, 23, 225; 1921, 25, 35; 1922, 27, 149; 1923, 29, 285); whilst Vernon (Trans. Far. Soc., 1927, 23, 169) has shown that differences in the physical condition of the specimens have no appreciable effect on their (atmospheric) corrosion.

† During all operations of this kind, the specimens are surrounded by paper covers to protect them from contamination.

‡ The specimens are stretched to a span of about 4 in. during exposure, so as to separate the adjacent loops. Details of the method of exposure are given in the Appendix.

§ The lowest resistance measured is 0·03 ohm; for an accuracy of 1 part in 10,000 the contact resistance must therefore be reproducible to 3 microhms.

The method was not, however, suitable for the preparation of a large number of specimens, owing to the high cost of production. The manufacture of specimens on a large scale was rendered practicable by a slight modification, suggested by Mr. L. H. Wadsworth (Messrs. L. H. Wadsworth, Pimlico, S.W.1). In this case the terminals are made from tape of the necessary cross-section, and the wire is fixed by punching the terminal with a blunt tool, as shown in *C*.

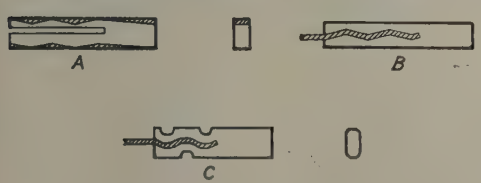


FIG. 1.—METHODS OF FIXING THE TERMINALS.

Method of Measurement.

The resistance of the specimens varies from about 0·03 to 2 ohms, according to the material. After careful consideration, the method shown diagrammatically in Fig. 2 was adopted for the resistance measurements. This is an ordinary Wheatstone bridge, which is balanced by shunting one or other of the ratio arms. The standard resistances P, Q, R were made to a special design, illustrated in Fig. 3, and are carefully calibrated from time to time.* Q and R have a range from 1 to 15 ohms, in steps of 1 ohm, and P from 0·1 to 1·5 ohms, in steps of 0·1 ohm. The resistance of the specimen X may be approximately followed by varying the standard resistances. For instance, if the bridge is balanced when $R=12$ and $Q=13$, $X=12P/13=0{\cdot}923P$. If, now, R and Q are changed to 13 and 14 respectively, the new equilibrium value of X is $13P/14=0{\cdot}929P$. The small gap between these two values can be covered by applying the shunt S, which is a four-dial switch resistance box, variable by steps of 0·1 ohm up to a total resistance of 1111 ohms. The

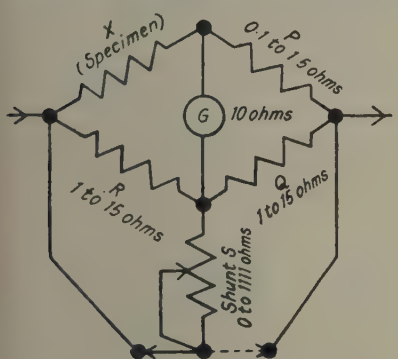


FIG. 2.—THE THEORETICAL CIRCUIT.

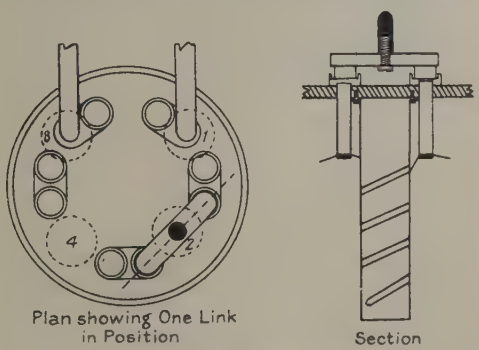


FIG. 3.—THE STANDARD RESISTANCES.

galvanometer G was obtained from Messrs. H. Tinsley, and has a resistance of 10·7 ohms, with a sensitivity of 51 mms. per microampere at one metre.

With this apparatus the resistance of the specimens over the range indicated can be measured with an accuracy of approximately 0·1 per cent.

* Each resistance comprises four coils of one, two, four and eight units, connected in series, any or all of which may be short-circuited by means of copper links dipping into mercury cups, as shown in the diagram.

The Experimental Bridge.

The apparatus used for the resistance measurements is illustrated in Figs. 4 and 5. The specimens are stretched between the mercury cups m, milled out to a depth of 10 mms. in the heavy copper blocks B, which are supported on a fibre base F. The cups, which are 9 cms. apart, are just a little larger than the terminals of the specimens, so that, when the latter are pushed down to the bottom, very good contacts are obtained. The copper blocks B are connected to the upper part of the bridge by five copper rods C, $\frac{1}{4}$ in. in diameter, which are riveted to the floors of the mercury cups M. The lower ends of the rods are amalgamated and dip into the mercury cups n. The two parts of the apparatus are thus detachable, but perfect

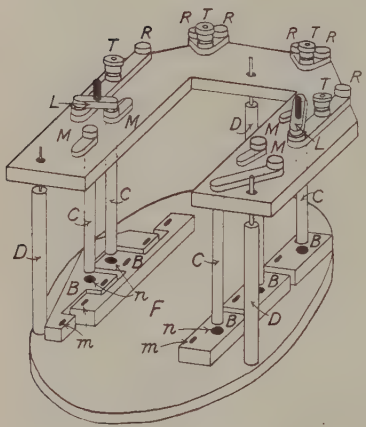


FIG. 4.—THE EXPERIMENTAL BRIDGE

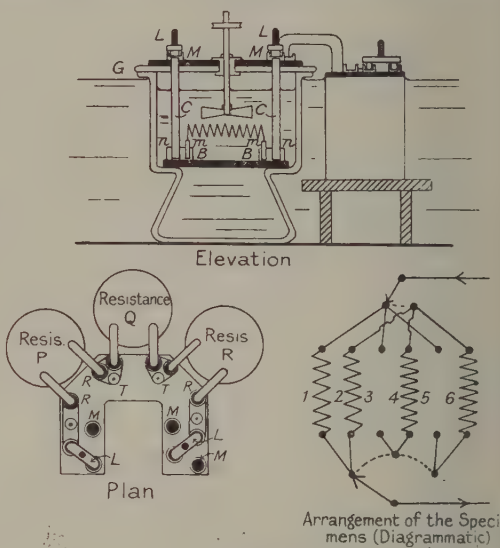


FIG. 5.—THE EXPERIMENTAL APPARATUS.

electrical connection between them is secured when they are clamped together by the distance pieces D.

The upper blocks and mercury cups are mounted on an ebonite panel, resting on a thick glass plate G. This plate forms the lid of a large desiccator full of acetone, and the specimens are completely covered by the liquid when the plate is placed in position. The desiccator itself is immersed to within an inch of the top in a large oil thermostat, fitted with the usual electrical heating and stirring devices. The terminals of the standard resistances fit into the mercury cups R, and the screw terminals T are used for the necessary connections to the batteries, galvanometer and the variable shunt.*

* The insulation of all the materials used (acetone, fibre, glass and ebonite) has been tested and found satisfactory. In the case of acetone, the least perfect insulator, the resistance across a 7 cm. gap between two thick leads to a " megger " was found to be 2·5 to 3 megohms at 500 volts.

When the bridge has been assembled, the specimens are left in the acetone bath, which is stirred by a small auxiliary stirrer, until the temperature is within a tenth of a degree or so of 25°C., and the resistance measurements are then made. (The nominal temperature for the resistance determinations is 25·00°C., but it has been found expedient to work at a temperature reasonably near this, and to apply a small temperature correction, since there is an appreciable lag between the temperature of the oil bath and that of the acetone.)

The measurements are made by adjusting the resistances P, Q, R, so that PR/Q is slightly greater than the resistance of the specimens, and reading off the values of the shunts, applied across R, that are necessary to balance the bridge when each specimen is introduced into the circuit in turn by means of the links L. The temperature of the acetone bath is also recorded, and the resistance of the specimens is calculated as described in the next section.

Methods of Calculating and Expressing the Results.

Since the effects of corrosion are deduced from the *percentage* change in the resistance of the specimens, it is not necessary to calculate their absolute resistance. The results may therefore be expressed in terms of an arbitrary unit R_0, which, for convenience, may be taken as PR/Q. The absolute resistance of the specimens at 25·00°C. is given by

$$X = R_0(1 - \alpha \times 10^{-4}),$$

where $\alpha \times 10^{-4}$ is a small factor. The value of R_0, of course, varies for each set of specimens.

As an illustration of the methods of calculating and expressing the results, the data for the initial measurements of a set of 19 S.W.G. copper coils are given in Table I. In this particular case P, Q, R were 0·1, 8 and 3 ohms respectively, so that the value of the arbitrary unit, R_0, was $0{\cdot}1 \times \frac{3}{8}$, or 0·0375 ohm. The values of the shunts applied across the 3-ohm coil necessary to balance the bridge are given in the second column. In the case of the first determination of the resistance of coil 1, the shunt was 52·80 ohms. The resistance of this coil is therefore

$$X = 0{\cdot}1 \times \frac{3}{8} \times \frac{52{\cdot}8}{52{\cdot}8 + 2{\cdot}99_0}*$$

$$= R_0\left(1 - \frac{2{\cdot}99_0}{55{\cdot}8}\right)$$

$$= R_0(1 - 536 \times 10^{-4}).$$

The temperature of the bath was 25·21°, and the corresponding temperature correction (to 25·00°)

$$-39 \times 10^{-4} \times 0{\cdot}21 = -8 \times 10^{-4}.$$

The corrected value of the resistance is thus

$$X = R_0(1 - 536 \times 10^{-4})(1 - 8 \times 10^{-4}),$$

$$= R_0(1 - 544 \times 10^{-4}).$$

* The corrected value of the 3-ohm resistance.

In this case $\alpha=544$; the corresponding values of α for the other specimens are given in the last column.

TABLE I.—*Determination of the Initial Resistance of* 19 *S.W.G.* (0·040″) *Copper Specimens.*
Unit $R_0=0{\cdot}1\times\frac{8}{3}$. Temperature coefficient for Copper 0·0039.
Initial Resistances.

Coil.		Shunt across 3 ohms for balance.	Temperature.	α (uncorrected).	Temperature correction.	α
I	1.*	$52{\cdot}8_0$	25·21°	536	−8	544
	3.	$52{\cdot}0_0$	25·21°	543	−8	551
	4.	93·3	25·21°	310	−8	318
	5.	74·9	25·21°	384	−8	392
II	1.	52·0	25·01°	544	Nil.	544
	3.	51·0	25·01°	554	Nil.	554
	4.	91·7	25·01°	316	Nil.	316
	5.	73·35	25·01°	391	Nil.	391
III	1.	52·1	25·02°	542	−1	543
	3.	51·05	25·03°	553	−1	554
	4.	91·4	25·04°	316	−2	318
	5.	73·45	25·05°	391	−2	393

The three series of determinations given in Table I were made independently on different days. The results are, therefore, a fair indication of the accuracy obtainable. The average deviation of the individual values from the mean is 1 part in 10,000, and, as a rule, the resistance measurements are reproducible with this accuracy.

TABLE II.—*Change in Resistance of* 19 *S.W.G. Copper Specimens after Seven Months' Exposure.*

Coil.	α (initial) mean of I, II, III.	α (final).	$\Delta\alpha$.	ΔR p.c.
1.	544	278	266	2·82
3.	553	286	267	2·83
4.	317	38	279	2·88
5.	392	380	12	0·12

Table II illustrates the effect of seven months' exposure on the resistance of the specimens. If α_I and α_F are the initial and final values of α, the percentage increase in resistance

$$(\alpha_I-\alpha_F)10^{-4}\times100/(1-\alpha_I\times10^{-4})$$
$$=(\alpha_I-\alpha_F)/(1-\alpha_I\times10^{-4})100.$$

The values of ΔR calculated in this way are given in the last column. The increase in resistance due to corrosion is equal to 2·84 (mean of the three exposed specimens) −0·12† (change in the "blank"), or 2·72 per cent. From this value the equivalent loss in weight of metal could be calculated as on page 109. Since, however, for a number of different materials the changes in resistance per cent. are directly

* The numbers refer to the position of the specimen in the bridge.

† In this particular case the increase in the "blank" was largely accounted for by slight changes in the standard resistances.

comparable, being equal to the percentage reduction in cross-section,* whereas the losses in weight are not (because they involve the density of the material, which may differ from one metal to another), there is usually no advantage in doing this, and the corrosion may be expressed directly in terms of the resistance change.

III. Experimental Results.

The experimental work that will now be described, was undertaken as a preliminary to a much more extensive series of field tests on the atmospheric corrosion of non-ferrous metals and alloys. The chief object of the experiments was to test the validity of the method rather than to obtain comparable data for different materials. The first necessity was to show that measurable resistance changes were produced in the metals on exposure, and the second that these changes were definitely proportional to the corrosion. The first object has been achieved by making a direct test on a wide range of non-ferrous metals and alloys, whilst the quantitative nature of the results has been investigated by observing the relationship between the resistance change and the diameter of the specimen, and also by a direct correlation of the increase in resistance and the corresponding change in weight of the same specimen.

Short Period Corrosion Tests on Typical Non-Ferrous Materials (*Winter*, 1926-27).

Fourteen sets of 22 S.W.G. (0·028 in.) specimens were exposed at the Royal Botanic Gardens, Regent's Park, where a site in the Meteorological enclosure was kindly provided by the Royal Botanic Society. The changes in the resistance of the specimens after 53 days' exposure, from November 18, 1926, to January 10, 1927, are given in Table III. Although the materials have been arranged in order of resistance change, this is not necessarily the true order of corrodibility, since, in the absence of any knowledge of the corrosion-time curve for the different materials, it would not be justifiable to base any conclusions as to their respective merits on the results of tests extending over such a limited period.

The results show conclusively that the resistance method can be successfully applied to a wide variety of materials. The average difference between the result for any one specimen and the mean for the series of three specimens of the same material is as low as 2 per cent. of the actual increase in resistance, which is very satisfactory accuracy for a " field test " on corrosion.

In order to test whether the corrosion product contributes to the conductivity, the resistance of the phosphor-bronze and the 60/40 brass specimens was redetermined after as much as possible of the corrosion product had been removed by scrubbing with a nailbrush, moistened in acetone. This did not produce any appreciable difference, and the corrosion product may therefore be assumed to be a non-conductor. (The " blanks " were also scrubbed.)

* If we assume that the corrosion film is of uniform thickness at all points, and also that there is a sharp boundary between the corrosion product and the uncorroded metal. Admittedly these conditions are only approximately obeyed in practice. The point is that, in comparative tests on different metals of widely different densities, such as copper, zinc and aluminium, it would probably be preferable to calculate the loss in volume of a standard specimen rather than its loss in weight. Under ideal conditions the relative increase in resistance is directly proportional to the loss in volume.

TABLE III.—*Exposure Tests at the Royal Botanic Gardens.*
Changes in Resistance of 22 S.W.G. Specimens after 53 Days' Complete Exposure.
(Winter, 1926/27.)

	R_0 Ohms.	Percentage Increase in Resistance.				
		Blank.	Exposed Specimens (Corrected for "Blank").			Mean.
1. 80/20 Copper-Nickel ...	1·15	0·04	1·42	1·52	1·53	1·49
2. Nickel I*	0·38	−0·04	1·61	1·69	1·72	1·67
3. Nickel II	0·38	0·00	1·68	1·72	1·80	1·73
4. Copper	0·08	−0·01	1·95	1·85	1·89	1·90
5. Phosphor-bronze ...	0·72	0·01	1·99	2·02	2·10	2·04
6. Nickel Silver (Seconds)	1·25	−0·11	2·15	2·12	2·15	2·14
7. 55/45 Copper-Nickel ...	2·15	0·04	2·08	2·17	2·22	2·16
8. 70/30 Nickel-Copper II*	2·10	0·00	2·34	2·34	2·47	2·38
9. 70/30 Nickel-Copper I	2·10	0·00	2·47	2·37	[3·00]†	2·42
10. Cadmium-copper (1 per cent. Cd.)	0·09	0·00	2·65	2·52	2·61	2·59
11. 70/30 Brass (As received)	0·28	−0·03	2·60	2·68	2·66	2·65
12. 70/30 Brass (Annealed)	0·28	0·03	2·81	2·87	2·97	2·88
13. 70/30 Brass (As received and fitted with soldered terminals) ...	0·28	−0·07	3·07	2·99	3·01	3·02
14. 60/40 Brass	0·30	0·00	3·64	3·84	3·88	3·79

EFFECT OF REMOVING PART OF THE CORROSION PRODUCT.
Increase in Resistance per cent. due to "Scrubbing."

	Phosphor-bronze.				60/40 Brass.		
Exposed Specimens	0·06	0·06	0·07	...	0·01	0·06	0·08
Blank		0·11		...		0·03	

The Effect of the Length of the Coil and of the Gauge of the Wire on the Resistance Changes Produced by Corrosion.

The relation between the resistance change produced by corrosion and the diameter of the wire was investigated by exposing copper specimens of four different gauges. Simultaneously with these tests, observations were also made on copper specimens of the same gauge, but comprising different lengths of wire. This was done to test whether any local corrosion occurred at the joints; in this case the percentage increase in resistance should be greater for the shorter specimens. The full list of specimens is given below:—

Series.	Number of Turns.	Length of Wire.	S.W.G.	Diameter.
		(Cms.)		(Ins.)
A	40	160	22	0·028
B	28	110	22	0·028
C	14	60	22	0·028
D	38	150	21	0·032
E	37	150	20	0·036
F	37	150	19	0·040

* (Table III.) Since nickel and the nickel-rich copper-nickel alloys can only be amalgamated with difficulty, these materials were fitted with terminals of copper-nickel alloys with a higher copper content. Two series were prepared in each case, (I) with 55/45 and (II) with 80/20 copper-nickel terminals respectively. No appreciable difference was observed in the resistance changes of the two sets of specimens and the procedure may therefore be considered justifiable.

† Specimen damaged.

A rather curious observation was made during the initial resistance measurements. Although duplicate determinations agreed well in the case of the coils with the full number of turns, there was a definite increase in the resistance of the shorter coils (Series B and C) from one determination to another. This is shown in Table IV,

TABLE IV.—*Variation in the Initial Resistance of Copper Specimens.*

Series A (40 turns. 22 S.W.G.). $R_0 = 0{\cdot}1 \times 8/10$. Values of α.

Date	9.7.26	9.7.26	12.7.26	Mean
A1	338	333	335	335
A3	335	329	331	332
A4	422	418	419	420
A5	313	311	312	312

Series B (28 turns. 22 S.W.G.). $R_0 = 0{\cdot}1 \times 5/9$. Values of α.

Date	9.7.26	10.7.26	12.7.26	13.7.26	15.7.26	18.7.26	Mean of last four
B1	329	320	318	310	311	319	315
B3	333	334	333	327	330	336	332
B4	398	392	390	388	390	395	391
B5	265	253	248	245	244	246	246

Series C (14 turns. 22 S.W.G.). $R_0 = 0{\cdot}1 \times 4/14$. Values of α.

Date	13.7.26	15.7.26	17.7.26	19.7.26	Mean of last three
C1	576	522	527	519	523
C3	972	953	956	952	954
C4	652	624	621	611	619
C5	787	760	766	763	763

Series D (38 turns. 21 S.W.G.) $R_0 = 0{\cdot}1 \times 6/10$. Values of α.

Date	14.7.26	16.7.26	19.7.26	Mean
D1	670	672	674	672
D3	947	944	945	945
D4	651	646	648	648
D5	536	532	535	534

Series E (37 turns. 20 S.W.G.). $R_0 = 0{\cdot}1 \times 4/9$. Values of σ.

Date	13.7.26	15.7.26	17.7.26	Mean
E1	67	68	68	68
E3	250	247	243	243
E4	203	200	200	201
E5	235	238	234	236

Series F (37 turns. 19 S.W.G.).* $R_0 = 0{\cdot}1 \times 3/8$. Values of σ.

Date	14.7.26	16.7.26	19.7.26	Mean
F1	544	544	543	544
F3	551	554	554	553
F4	318	316	318	317
F5	392	391	393	392

* See also Table I.

where a complete list of all the determinations, in chronological order, is given, After a few days the resistance of the shorter coils also reached a constant value. The variation in resistance is probably due to the stretching of the specimens, which leads to a permanent " set " in the case of the shorter specimens. (It will be remembered that when the specimens are prepared all the loops are touching each other, but that these are pulled apart during measurement and exposure. Incidentally, the " blanks " are stored in the stretched condition.) Although this variation in resistance has never been observed in specimens with the full number of turns,

it is advisable to anneal them in the fully stretched condition, so as to minimise the effects of any subsequent stretching. This has been done in the later work.

The specimens were exposed on the roof of the Royal School of Mines at South Kensington. The stand used to support the specimens is described in the Appendix. Exposure was begun on July 21, 1926, and the tests are still in progress. The increase in the resistance has since been determined on three occasions :—

1. On October 30, 1926, after 101 days' exposure.
2. On March 1, 1927, after 213 days' exposure ; and
3. On August 23, 1927, after 381 days' exposure.*

The complete results are given in Table V, and the mean increase in resistance

TABLE V.

Increase in the Resistance of Copper Specimens on Exposure to the South Kensington Atmosphere.

Gauge.	Speci-men.	Percentage Increase in Resistance. Oct. 30, 1926. 101 Days.	Mar. 1, 1927. 213 Days.	Aug. 23, 1927. 381 Days.	Gauge.	Speci-men.	Percentage Increase in Resistance. Oct. 30, 1926. 101 Days.	Mar. 1, 1927. 213 Days.	Aug. 23, 1927. 381 Days.
22	A1	0·93	4·07	4·97	21	D1	0·67	3·60	4·50
S.W.G.	A3	0·91	4·02	4·86	S.W.G.	D3†	0·11	0·05	0·04
(160	A4	1·04	4·22	5·11	(150	D4	0·73	3·85	4·86
cms.).	A5†	0·08	0·12	0·14	cms.).	D5	0·71	3·74	4·74
22	B1	0·90	4·22	5·23	20	E1†	0·07	0·06	0·01
S.W.G.	B3†	0·12	0·09	0·13	S.W.G.	E3	1·01	3·37	4·04
(110	B4	0·76	4·26	4·86	(150	E4	0·80	3·41	4·24
cms.).	B5	0·90	4·56	5·60	cms.).	E5	0·99	3·58	4·38
22	C1	0·91	4·20	5·10	19	F1	0·49	2·82	3·62
S.W.G.	C3†	0·08	0·03	0·04	S.W.G.	F3	0·46	2·83	3·65
(60	C4	0·93	4·46	5·33	(150	F4	0·47	2·88	3·81
cms.).	C5	[1·52]	[5·15]	[6·19]	cms.).	F5†	0·12	0·12	0·20

for each series (i.e., the average for the three exposed specimens, less the change in the " blank ") is shown in Table VI. Table VII illustrates the effect of the gauge

TABLE VI.—*Corrected Mean Values of the Percentage Increase in Resistance.*

Series.	Percentage Increase in Resistance. 101 days.	213 days.	381 days.
A	0·88	3·99	4·82
B	0·73	4·26	5·10
C‡	0·84	4·30	5·18
D	0·59	3·68	4·66
E	0·86	3·39	4·21
F	0·35	2·72	3·49

* The periods stated do not include the few days during which the specimens were undergoing examination in the laboratory.

† Blank stored in the Laboratory.

‡ Mean of two specimens only.

TABLE VII.—*The Effect of Gauge on the Resistance Change.*

Series.	Diameter (in.)	Relative diameter *d*.	101 days. Per cent. increase in resistance ΔR.	101 days. $\Delta R \times d = K$.	101 days. Per cent. deviation of K from Mean.	213 days. Per cent. increase in resistance ΔR.	213 days. $\Delta R \times d = K$.	213 days. Per cent. deviation of K from mean.	381 days. Per cent. increase in resistance ΔR.	381 days. $\Delta R \times d = K$.	381 days. Per cent. deviation of K from mean.
A	0·028	7	0·88	6·2	+13	3·99	27·9	−3·1	4·84	33·9	−5·6
D	0·032	8	0·59	4·7	−15	3·68	29·4	+2·1	4·66	37·3	+3·6
E	0·036	9	0·86	7·7	+40	3·39	30·5	+5·9	4·21	37·9	+5·3
F	0·040	10	0·35	3·5	−36	2·72	27·2	−5·6	3·49	34·9	−3·1
			Mean	5·5		Mean	28·8		Mean	36·0	

TABLE VIIA.—*Results after* 541 *Days' Exposure.*

Series.	Percentage increase in resistance. 1.	3.	4.	5.	Mean value corrected for blanks. ΔR.	Relative diameter *d*.	$\Delta R \times d = K$.	Per cent. deviation of K from mean.
A	6·78	6·69	6·99	0·14	6·68	7	46·8	−5·4
D	6·03	0·05	6·54	6·52	6·31	8	50·5	+2·0
E	0·03	5·40	5·74	5·79	5·61	9	50·5	+2·0
F	5·07	5·15	5·49	0·24	5·00	10	50·0	+1·0
B	7·17	0·09	6·74	7·54	7·06	Mean	49·5	
C	7·30	0·00	7·50	[8·43]	7·40			

on the resistance changes, and gives the values of the product K of the percentage increase in resistance and the relative diameter of the wire. Theoretically, K should be constant for all four gauges of wire at any given period. It will be seen that this is the case with the exception of the results for the first period of exposure. The individual values of K for the later periods are, on the average, within 5 per cent. of the corresponding mean values for the four gauges of wire. This figure is comparable with the probable experimental error.*

The results of this experiment show that the resistance change is inversely proportional to the diameter. It is therefore possible to use the electrical resistance method as an "acceleration test" by conducting tests on relatively thin wires, since the changes produced in the thicker wires used in practice can be calculated from the results of the experiment by simple proportion. In this respect the method constitutes an acceleration test of an ideal type, having the great advantage over many previous tests of this kind that the increased rate of attack is not obtained by exposing the specimens to artificial conditions, often radically different to those encountered in practice. On the contrary, the medium of exposure is unchanged, and the acceleration is produced by choosing the geometrical shape of the specimen in such a way that corrosion produces a maximum effect. In view of the present demand for accelerated corrosion tests in industry, it may be permissible to urge that this is by far the soundest way to diminish the time necessary for an experiment.

The anomalous results observed after the first hundred days' exposure may be partly due to slight structural differences between the extreme surface layer of the wire and the core. If the surface layer is attacked at a different rate from the body of the wire, the erratic results obtained in the initial stages of attack might be explained by assuming that this layer had a slightly different thickness in the different specimens.

It is interesting to note that these corrosion tests in the open show a seasonal variation in the rate of attack, similar to that which has already been observed when the specimens are exposed in a Stevenson screen.† This may be illustrated by calculating the mean daily increase in the value of the constant K for the four periods of exposure.

Period.	Value of K.	Increase.	Days.	Increase per day.
July-October, 1926 (summer) ...	5·5	5·5	101	0·055
November, 1926 March, 1927 (winter)	28·8	23·3	112	0·280
March-August, 1927 (summer) ...	36·0	7·2	168	0·043
August, 1927 February, 1928 (winter)	49·5	13·5	160	0·084

The rate of corrosion in winter is thus appreciably greater than in summer, although the difference between the two periods is not so pronounced as in the case of Stevenson screen exposure, where the ratio of the rates of attack may vary from

* (Added February 10, 1928.) A redetermination of the resistance of the specimens on February 3, 1928, after 541 days' exposure, gave the values shown in Table VIIA. It will be seen that the values of K for the four gauges of wire are in even better agreement than in either of the earlier periods of exposure.

† Trans. Far. Soc., 23 (1927), 184.

six to thirteen, according to the material. This large difference in the corrosivity of the atmosphere is no doubt due to the increased pollution and greater humidity during the winter.

As regards the effect of the length of the coil on the resistance changes, the agreement between the results for the different specimens is sufficiently good to show that there is no appreciable local corrosion at the joints. Indeed, the slight differences observed, amounting to less than 8 per cent., may not be due to this cause at all, but rather to a closer packing of the loops in the longer coils, leading to a mutual protective effect, and in consequence to a reduced rate of corrosion.*

Correlation of Weight Increment and Resistance Change (Stevenson Screen Exposure).

The validity of the resistance method for studying corrosion may be tested by a direct observation of the weight changes of the specimens on which the resistance determinations are made. This is most conveniently done when the specimens are exposed in a Stevenson screen. In this case the increase in weight of the specimens can be readily determined ; moreover, if the positions of the specimens in the screen are suitably chosen, it is possible of obtain a series of different weight increments for specimens exposed simultaneously, since the intensity of corrosion decreases from the bottom of the screen upwards.†

The first tests were made on 22 S.W.G. (0·028 in.) specimens : two sets of copper, one of 80/20 copper-nickel and one of phosphor bronze. In order to obtain as many points as possible on the weight-increment/resistance change curve, no " blanks " were kept and all the specimens were exposed. After the initial resistance measurements, the amalgam was removed from the terminals and the specimens were weighed. They were then exposed for a suitable period in a Stevenson screen on the roof of the Royal School of Mines. This was followed by a second weighing and a final resistance determination.

The results obtained are given in Table VIII, and the data are plotted in Fig.6. In all four cases the results are in fairly good agreement with a linear relationship between weight increment and resistance change, as demanded by theory. The straight lines should, however, pass through the origin, since zero weight increment should correspond to zero resistance change. In the absence of " blanks," it is not advisable to form any conclusions on this point, although the intercepts on the resistance change axis are probably too large to be attributed solely to experimental error.

* The actual distance between two loops is approximately given by

$$\delta = \frac{3{\cdot}5 - nd}{n - 1}$$

where n equals the number of turns and d equals the diameter of the wire. If the necessary calculations are made, the following values of δ are obtained :—

Series A	...	δ=0·061 in.	Series D	...	δ=0·062 in.
B	...	0·101	E	...	0·060
C	...	0·239	F	...	0·058

† This is due to the fact that most of the air enters by the bottom of the screen. Full details of the method of exposure in a Stevenson screen are given in the Meteorological Magazine, 62, 53 (1927).

TABLE VIII.—*Correlation of Weight-Increment and Resistance Change (Stevenson Screen Exposure).*
(22 S.W.G. specimens.)

Metal.	Specimen.	Weight-increment. Mgms.	Resistance change per cent.	
			Observed.	Calculated.
Copper I.	1	56·4	0·62	0·45
Exposed for 77 days,	3	81·4	0·82	0·65
October-December, 1926.	4	65·9	0·69	0·52
P=31 per cent. Cu.	5	30·0	0·37	0·24
Copper II.	1	61·3	0·76	0·38
Exposed for 55 days,	3	115·4	1·11	0·72
October-December, 1926.	4	62·5	0·71	0·39
P=26 per cent. Cu.	5	29·1	0·46	0·18
Phosphor Bronze.	1	65·1	0·94	0·49
Exposed for 41 days,	3	49·2	0·77	0·37
November-December, 1926.	4	91·4	1·16	0·69
P=28 per cent. Cu, 2 per cent. Sn.	5	29·1	0·59	0·22
80/20 Copper-Nickel.	1	111·4	1·12	1·15
Exposed for 48 days,	3	95·5	0·94	0·99
November, 1926-January, 1927.	4	131·0	1·21	1·35
P=30 per cent. Cu, 7 per cent. Ni.	5	77·6	0·95	0·80

Theoretical values for the resistance change, corresponding to the observed weight increments, can be calculated if the percentage of metal in the corrosion product is determined by analysis. If the weight increment of the specimen is S, and the corrosion product contains P per cent. of metal, the weight of metal corroded is $W=SP/(100-P)$, since a weight increment of $(100-P)$ gms. would result from the corrosion of P gms. of metal. The corresponding values of the resistance change may then be calculated by equation (3) on page 109.

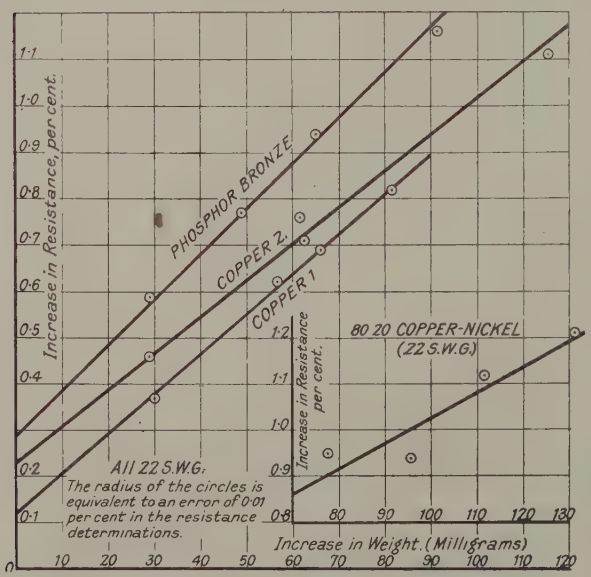

Increase in Resistance, per cent.
PHOSPHOR BRONZE
COPPER 2.
COPPER 1
80 20 COPPER-NICKEL (22 S.W.G.)
Increase in Resistance per cent.
All 22 S.W.G.
The radius of the circles is equivalent to an error of 0·01 per cent in the resistance determinations.
Increase in Weight. (Milligrams)

FIG. 6.—CORRELATION OF WEIGHT INCREMENT AND RESISTANCE CHANGE (Stevenson Screen Exposure).

The observed and calculated values of the resistance change are given in Table VIII. (For the specimens under

consideration, $A=36$ cm.^{2}, $r=0{\cdot}0355$ cm., and D was taken as 8·9 throughout.) It will be seen that both are of the same order of magnitude, but that the calculated figures are, on the whole, lower than those observed. This is not surprising, since the calculated figures necessarily represent minimum values of the possible resistance change for two reasons: First, any departure from ideal conditions—the uniform film of corrosion product—would lead to an increased resistance change per unit weight increment; secondly, the values of P found by analysis are almost certainly too low, since it is not possible to remove all the corrosion product, and the layer closest to the metal, which remains undetached, probably contains a higher percentage of metal. On the other hand, the *slopes* of the straight lines agree fairly well with the theoretical values.

Percentage Increase in Resistance per Mgm. Weight Increment.

——	Observed.	Calculated.
Copper I	0·0088	0·0079
Copper II	0·0078	0·0062
Phosphor bronze	0·0093	0·0076

(The figures for the 80/20 Copper nickel alloy are too erratic to be used for this calculation.)

The approximately linear relationship between weight-increment and resistance change has been confirmed by similar experiments on twelve 18 S.W.G. (0·048 in.) "silicon bronze"* specimens, in which the usual "blanks" were kept. The results after 96 and 157 days' exposure are shown in Figs. 6A and 6B respectively.†

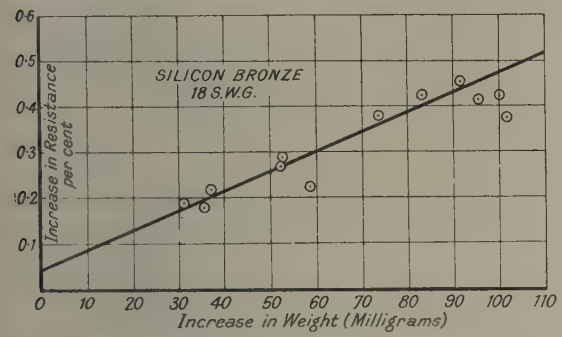


FIG 6A.—CORRELATION OF WEIGHT INCREMENT AND RESISTANCE CHANGE.
Result for "Silicon Bronze" after 96 Days' Exposure.

The encouraging feature of the results is the regular relationship between weight-increment and resistance change. The changes produced by corrosion in a metal are so complex that two different methods cannot be expected to give the same quantitative interpretation of its results; the fact that an approximate agreement is reached may be considered satisfactory. The results show that the resistance increases regularly with corrosion. Any irregularities due to pitting or other causes must therefore be of secondary importance,

* Copper with 0·8 per cent. of tin and 0·7 per cent. of zinc.

† Fig. 6B was added on February 10, 1928. It should be pointed out that the linear relationship between resistance change and weight increment cannot be expected to persist in the later stages of corrosion, because, owing to the condensation of moisture from the atmosphere, a saturated solution of corrosion product collects on the lowest parts of the specimens, thus affording every facility for intense local corrosion This may be the cause of the two anomalous results shown in Fig. 6B.

since the effect of a pit of dimensions comparable with the diameter of the wire would be to produce a large increase in resistance for a negligible increase in weight.

Correlation of Change in Weight and Resistance Change for Fully Exposed Specimens.

The correlation of resistance change and change in weight may also be carried out in the open, although in this case the experimental difficulties are much greater. The weight of metal corroded may be determined by applying a correction for the metal removed by the rain water, as in Vernon's experiments.* Let S be the observed increase in weight of the specimen itself, and E the weight of metal, per specimen, found in the rain water. If the metal removed by the rain were replaced on the specimen, an increase in weight equal to $E+S$ would be observed. This figure, therefore, represents the weight of non-metallic radicles contained in the corrosion product *on the specimen*, and if the percentage of metal in this corrosion product is P, the weight of corroded metal remaining on the specimen is $P(E+S)/(100-P)$. The total weight of metal corroded is thus $W=E+P(E+S)/(100-P)$. This value of W may be used to calculate the resistance change of the specimen, by the method already described.

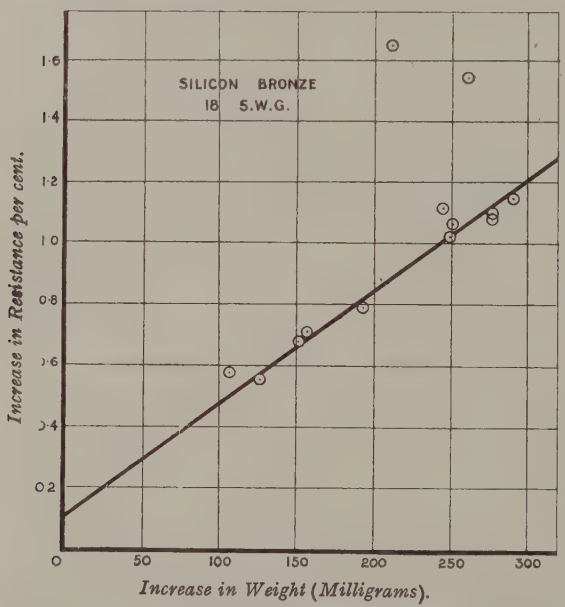


FIG. 6B.—CORRELATION OF WEIGHT INCREMENT AND RESISTANCE CHANGE.
Results for "Silicon Bronze" after 157 Days' Exposure.

Tests of this kind have been made on copper, nickel, 60/40 brass and 80/20 copper-nickel specimens, fully exposed on the roof of the Royal School of Mines. The wires used were 0·036" (20 S.W.G.) in diameter and 160 cms. long. The resistance measurements and the determination of the change in weight of the specimens were made in the same way as for the Stevenson screen experiments. During exposure the specimens of each material were supported over a separate enamelled pail, in which the rain water falling from the specimens was collected. At the end of the tests the amount of the respective metals in this rain water was determined. The analyses were complicated by the large volume of water collected (from 6 to 7 litres), and by the presence of considerable quantities of soot and other wind-blown

* W. H. J. Vernon, Trans. Far. Soc., 23, 166 (1927).

pollution, which contained both iron and aluminium oxides. The specimens were exposed for 168 days, from March 2 to August 17, 1927.

The percentage increase in resistance and the weight changes of the specimens are given in Tables IX and X, whilst the observed and calculated values of the resistance change are compared in Table XI. In the case of the two pure metals

TABLE IX.—(*Correlation of Change in Weight and Increase in Resistance for Fully Exposed Specimens*). *Values of the Percentage Increase in Resistance.*

—		Copper.	80/20 Copper-Nickel.	Nickel.	60/40 Brass.
Exposed Specimens	1	1·14	1·36	1·88	2·40
	2	1·15	1·39	1·92	2·25
	3	1·16	1·44	1·88	2·32
Mean		1·15	1·40	1·89	2·33
Blank		−0·02	0·06	0·00	−0·10
Net change ...		1·17	1·34	1·89	2·43

TABLE X.—*Change in Weight of the Specimens* (*Grams*).

—	Copper	80/20 Copper-Nickel.	Nickel.	60/40 Brass.
1	+0·0222	+0·0076	−0·0681	+0·0248
2	0·0231	0·0072	−0·0683	0·0181
3	0·0226	0·0112	−0·0701	0·0193
Mean	+0·0226	+0·0087	−0·0688	+0·0207

and the 80/20 copper-nickel alloy the results are in substantial agreement, the observed value being slightly the higher, which is understandable for the reasons already discussed. There is, however, a marked difference in the case of 60/40 brass, where the observed value is much lower than the calculated one. It is not advisable to discuss the matter very fully until further data are available, but there is nothing improbable in the result. Bengough and May have shown that the zinc present in solid solution is capable of reacting with the corrosion product of the brass to deposit metallic copper,* and similar examples of the "dezincification" of brass by atmospheric corrosion have been given by Vernon.† In the present case the results of the analyses support the view that copper has been re-deposited, since the 0·2041 gm. of zinc found in the corrosion product was originally associated with 0·3062 gm. of copper, whereas only 0·1122 gm. of copper was recovered. If this is so, the condition that the corrosion product should be a non-conductor is no longer fulfilled, and it is quite conceivable that the re-deposition of copper would cause a diminution of the observed increase in resistance.

The correctness of this view has been supported by the results of some tensile tests on these wires, which were kindly made by Mr. W. E. Alkins, M.Sc., in the

* G. D. Bengough and R. May, J. Inst. Met., 32, 149 (1924).
† W. H. J. Vernon, Trans. Far. Soc., 23, 170 (1927).

TABLE XI.—*Observed and Calculated Values of the Resistance Change.*

Metal.	S	E	$E+S$	P	$P(E+S)/(100-P)$	W	D	Resistance change.	
								Calculated from W.	Observed.
Copper ...	+0·0226	0·0232	0·0458	52·8	0·0512	0·0744	8·9	0·83	1·17
80/20 Copper-Nickel	+0·0087	Cu 0·0189 Ni 0·0197 0·0386	0·0473	Cu 58·6 Ni 0·7 59·3	Cu 0·0680 Ni 0·0008 0·0688	Cu 0·0869 Ni 0·0205 0·1074	8·9	1·20	1·34
Nickel ...	−0·0688	0·1227	0·0539	16·1	0·0103	0·1330	8·8	1·50	1·89
60/40 Brass ...	+0·0207	Cu 0·0088 Zn 0·1751 0·1839	0·2046	Cu 30·7 Zn 8·6 39·3	Cu 0·1034 Zn 0·0290 0·1324	Cu 0·1122 Zn 0·2041 0·3163	8·4	3·73	2·43

Research Laboratories of Messrs. T. Bolton & Sons, Ltd., at Oakamoor, N. Staffs. The breaking loads of the unexposed and exposed wires are shown in Table XII ;

TABLE XII.—*Decrease in the Breaking Load on Exposure.*

Metal.	Breaking load (lbs.).		Decrease.	
	Unexposed.	Exposed.	Lbs.	Per cent.
Copper	40	40	Too small to be detected.	
80/20 Copper-Nickel	60·2	58 8	1·4	2·3
Nickel	76·0	73·6	2·4	3·2
60/40 Brass	62·0	58·0	4·0	6·5

each figure represents the mean of nine or more determinations. The percentage decrease in the breaking load of the brass is in much better agreement with the change in weight, and confirms the view that the observed resistance change is too low. It is interesting to note that the order of corrodibility of the four materials is the same, whether the comparison is based on the loss in weight, the resistance change, or the decrease in breaking load.* The tensile tests were made on a 1000 lbs. machine reading to 1 lb., which does not appear to have been sensitive enough to detect the small change in the breaking load of the copper specimens.

The analyses of the 80 20 copper-nickel alloy seem to show that there is a tendency for the copper to accumulate on the specimen. perhaps owing to a selective solution of the nickel salts in the corrosion product by the rain water. This may be associated with the brown colour that develops on this alloy during exposure. There does not, however, appear to have been any marked copper re-deposition, since the two metals are fairly well balanced in the total corrosion product represented by *W*.

IV. Conclusion.

The main object of this Paper has been to describe a new, and perhaps more accurate, method of studying corrosion in the field. In experiments of this type it is difficult to obtain the rigorous agreement that is reached in more academic researches. When this difficulty is taken into consideration, it may be claimed that the results reported in this Paper show that the resistance method is directly applicable as a quantitative test of the atmospheric corrosion of metals. No doubt the method will be found to have its limitations—an indication of these may already have been seen in the case of the brass specimens discussed in the last section—but any corrosion test that can be applied quantitatively on a large scale under actual service conditions must undoubtedly be of practical value.

A series of tests by the electrical resistance method has been included in the field tests on atmospheric corrosion that were begun in June, 1927, by the Atmospheric Corrosion Committee of the British Non-Ferrous Metals Research Association at five stations in this country representative of rural, suburban, urban, industrial and marine atmospheres respectively. Admittedly some caution will be necessary in interpreting the results. For instance, it be will advisable to establish the shape of the corrosion time curve for each material investigated before any comparisons may be based on the results of exposure tests over a limited period.

* It should be clear that this " order of corrodibility " can only apply to the given experimental conditions.

Further experiments on the effect of gauge on resistance change will also be necessary to establish the law of similarity in each case, if the results obtained for thin wires are to be applied to the same materials in bulk. Subsidiary tests on the lines indicated in this Paper are, however, being continued, and extended to include a wider range of materials, and there is every reason to hope that the information obtained in this way will permit of an accurate interpretation of the results of the main tests when these are concluded.

Acknowledgments.

The author is indebted to the Council of the British Non-Ferrous Metals Research Association for permission to publish this Paper. He would like to express his appreciation of the very kind manner in which Prof. H. C. H. Carpenter, F.R.S., has supervised the work, of the encouragement and assistance which he has received from Dr. R. S. Hutton and Dr. O. F. Hudson, of the British Non-Ferrous Metals Research Association, and of the valuable advice given him by his colleague, Dr. W. H. J. Vernon, throughout the work. He would also like to thank Prof. A. O. Rankine, O.B.E., D. Sc., and Miss M. Bell, of the Physics Department of the Royal College of Science, for the loan of apparatus with which he was able to make some preliminary measurements.

Finally, acknowledgments are due to the Committee of the Royal Botanic Society of London for their kindness in providing a site for the exposure tests in their gardens, to the Director of the Meteorological Office for the loan of a Stevenson screen, and to Messrs. Thomas Bolton & Sons, Ltd., who kindly provided the copper, brass and bronze wires used in this work.

Metallurgical Department,
Royal School of Mines, S.W.7.
October, 1927.

V. Appendix.

Design and Calibration of the Stands Used for Outdoor Exposure.

Since the corrosion of a specimen is largely determined by the volume of air circulating over it, it is necessary to pay considerable attention to the design of the stand used for exposure, so as to ensure that all the positions in the stand are equivalent in this respect.

The stand installed on the roof of the Royal School of Mines, and used for the tests described on page 116, consists essentially of four wooden frames, made from $\frac{1}{2}$ in. square rod. The overall dimensions of these frames are 20 in. by $12\frac{1}{2}$ in., and each accommodates three rows of specimens, as shown in Fig. 8. The frames are supported in a horizontal position at different heights from the ground, so as to minimise any possible protection of one set of specimens by another. The stand was calibrated by determining the weight increments of a number of specimens of three different metals, which may be referred to as *A*, *B* and *C*. The distance between neighbouring specimens was varied from one frame to another to ascertain whether there was any mutual protective effect on the part of the specimens. In view of the labour involved, it was thought sufficient to weigh a selection of the exposed specimens, and to fill the remaining positions with similar dummy coils.

The weight increments after 14 days' exposure are shown in Fig. 7. It will be seen that the packing of the specimens has no perceptible effect on corrosion.

Stand used for the Resistance Tests.

The Exposure Station at the Royal Botanic Gardens, Regent's Park.
Fig. 8.

To face page 128

(The abnormal results at the ends of some of the rows are due to interference by the woodwork of the stand.) There is, however, a great difference between the results obtained at the back and front of the stand respectively. Thus, the average weight increment of the *B* coils in the right-hand frame near the railings is 29 mgms., whilst the corresponding figure for the specimens in the back left-hand frame is 19 mgms. The difference is probably due to the position of the stand at the edge of the roof, as a result of which the specimens at the back are more sheltered from the wind beating against the wall of the building. A roof is, therefore, not an ideal site for carrying out comparative corrosion tests, unless it is sufficiently wide to enable the specimens to be placed at a reasonable distance from the edge. In the present case it is doubtful if these local disturbances could be completely eliminated, and consequently the most recent experimental work has been carried out in the Royal Botanic Gardens, Regent's Park, where much more uniform conditions of exposure are obtained.

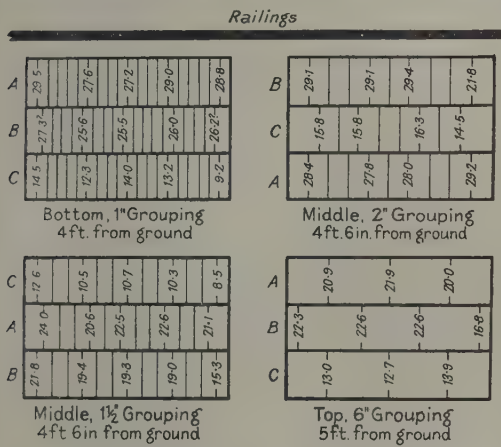


FIG. 7.—CALIBRATION OF THE STAND ON THE ROOF OF THE ROYAL SCHOOL OF MINES.

A new type of stand has also been designed, in which any interference by the material of the stand itself is reduced to a minimum. The specimens are exposed on wooden frames of $\frac{1}{2}$ in. square rod, 4 in. wide, by pushing the terminals into holes drilled in the wood. These frames are bolted to two triangular brackets made of $\frac{1}{2}$ by $\frac{3}{16}$ in. flat iron, as shown in Fig. 8. (The whole stand is, of course, adequately painted.) The lowest frame is 4 ft. 9 in. from the ground, and there is a vertical and horizontal clearance of about 3 in. between adjacent frames. The results of a calibration of the stand, given in Fig. 9, show that all the positions in the stand are equivalent within the limits of the experimental error.

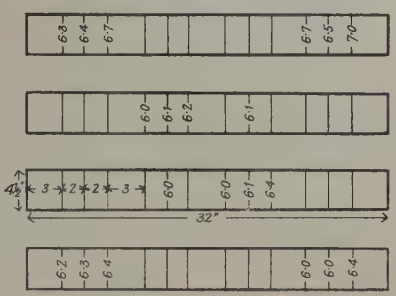


FIG. 9.—CALIBRATION OF THE STAND AT THE ROYAL BOTANIC GARDENS.
(The figures are the weight increments of copper specimens after 21 days' exposure in May, 1926.)

DISCUSSION.

Mr. J. H. COSTE said that the Author's method struck him *prima facie* as being satisfactory, unlike certain methods in which attempts were made to scrape off the corroded metal. Had the Author any data as to the composition of the air to which the specimens had been exposed?

Information on this subject could no doubt be obtained from the relevant committee of the D.S.I.R.

Dr. E. H. RAYNER said that some time ago he had advised the Author against the use of bridge methods, on account of secular change in the resistance of wire joints; but the Author had overcome this difficulty with excellent results by means of the new method of jointing he had described. Had he allowed for the effect of thermal E.M.F., which in the case of copper-nickel alloys would be material in such precise measurements as those described? Difficulty is often experienced in obtaining a definite area of contact between mercury and a copper rod dipping into it. Varnishing of the copper does not help matters, but no difficulty arises if the copper be nickel-plated. It would be advantageous to include the annealing temperatures in the Paper for future reference. As the tests occupied a considerable period of time, it must be borne in mind that secular changes might occur in the standard resistances in the bridge.

Dr. R. S. HUTTON, on behalf of the Non-Ferrous Metals Research Association, expressed appreciation of the encouragement given to the Author by the Physical Society's publication of his Paper. The problem of corrosion was so complicated that it would be most valuable to have a simple method applicable under widely varying conditions, like that described by the Author.

Dr. W. H. J. VERNON said that he had watched the work with great interest, and was impressed by the Author's accuracy and thoroughness. While the Society would be mainly interested in the method as such, from an economic point of view the important matter would be its application in obtaining corrosion data under a wide range of conditions. Arrangements were being made for observations at six stations engaged in research on atmospheric pollution. The method of accelerating results by reducing the diameter of the specimens was much superior to methods in which artificial corrosion was produced, since the results of the latter bore little relation to natural corrosion. Caution was necessary, since the later course of a corrosion process could not be inferred from its earlier stages; thus arsenical copper, for instance, is at first more rapidly corroded, but after long exposure much less so, than pure copper.

The AUTHOR, in reply, thanked Dr. Rayner for the suggestion as to the use of nickel-plated copper for the mercury contacts. He had eliminated the effect of thermal E.M.F. by adopting a careful routine, and had re-calibrated the standard resistances from time to time, in addition to using unexposed blanks as controls. By arrangement with Dr. J. S. Owens, the field work would be associated with the research which is being carried out on atmospheric pollution.

Prof. E. WILSON (communicated): I am very pleased to see a Paper by Mr. Hudson on the Atmospheric Corrosion of Metals, and appreciate the invitation to contribute to the discussion. On reading the Paper through I am still in difficulty as to how the variation in specific resistance due to exposure is to be allowed for in the absence of direct experiment. The following figures are taken from a Paper read before the Society,* and refer to specimens of high purity aluminium and duralumin, both of which were exposed to London atmosphere for eight years. If R_0 R_t were the electrical resistances of the wires at the commencement and at time t during exposure, ρ_0 ρ_t the corresponding specific resistances, a_0 a_t the corresponding cross-sectional areas, it follows that the ratio $R_t/R_0 = \rho_t/\rho_0 \times a_0/a_t$. It will be seen that the ratio a_0/a_t is much greater in the case of the high purity aluminium, and yet the ratio R_t/R_0 is the same for each specimen. If, therefore, the amount of corrosion is to be inferred from the change in resistance, it becomes a question as to whether the correction due to the change in resistance of the control specimen, which had been stored in the laboratory, could allow of the ratio a_0/a_t being determined with fair accuracy. The control specimens stored in the laboratory were tested, and it will be seen that no change was found in the case of the high purity aluminium, and the duralumin diminished in specific resistance. Whereas in the case of each of the exposed specimens the ratio ρ_t/ρ_0 was increased, the increase being greater in the duralumin.

——	Time t in years.	Unexposed.	Exposed.		
		ρ_t/ρ_0	ρ_t/ρ_0	a_0/a_t	R_t/R_0 observed.
High purity aluminium	8	1·00	1·061	1·127	1·15
Duralumin	8	0·954	1·109	1·038	1·15

* Proc. Phys. Soc., 39, 15 (1926).

It might be worth while placing the control specimen in a tube filled with an inert gas and subjecting it to the same temperature changes as the exposed specimens in order to see if a better agreement could be obtained. I am glad to see that the Author has increased the diameter of the exposed conductors, and I should like to ask if special attention has been given to the possibility of error due to thermo-electromotive forces. In conclusion, I should like to congratulate the Author on his Paper, and I look forward to further contributions to what is admittedly a difficult subject.

AUTHOR'S reply: Prof. Wilson's chief point seems to be that changes may occur in the specific resistance of the exposed specimens, which will not be compensated for by observing the changes in resistance of similar specimens stored in the laboratory. His views are based on observations of the specific resistance of certain aluminium alloys before and after exposure. The final measurements were made after scraping off the corrosion product. Prof. Wilson will probably agree that the accuracy obtainable by this method is not very great, particularly in the case of an $\frac{1}{8}$-inch wire, as used in his experiments, so that the values of ρ_t/ρ_0 deduced in this way cannot be regarded as conclusive. He was perhaps unfortunate in having to deal with complicated alloys like duralumin, some of which are subject to age hardening, and presumably, therefore, to secular changes in resistance. In these cases one would expect the apparent specific resistance to increase on exposure, since Prof. Wilson's method of measuring the final resistance would not eliminate the effects of intercrystalline corrosion, to which some of these alloys are particularly susceptible. In the present investigation, however, the fact that the observed resistance changes agree with the values calculated from the accompanying changes in weight of the specimens shows that there can be no appreciable variation in the specific resistance of the materials.

It is conceivable, however, that in certain complicated alloys resistance changes might occur as a result of exposure outdoors quite apart from those due to corrosion, and I therefore agree with Prof. Wilson's kind suggestion as to the advisability of exposing the "blanks" to the same temperature changes as the exposed specimens, and I hope to test the matter experimentally in the near future.

XVII.—SOME METHODS OF ESTIMATING THE INTENSITIES OF SPECTRAL LINES.

By W. H. J. Childs, *B.Sc.*, Demonstrator in Physics, King's College, Strand.

Received December **16, 1927.**

(Communicated by Prof. O. W. Richardson, F.R.S.)

Abstract.

This Paper presents a critical account of several methods of spectral photometry applied to the special case of the band spectrum of helium. With the method finally adopted, the line spectrum is photographed in the usual way, after which the plate has to be calibrated. To do this the slit of the spectroscope is illuminated in a special manner by a tungsten filament lamp, so that upon development the plate exhibits a number of images of continuous spectra of progressively increasing density. From these images may be ascertained (*a*) the relation between intensity of light and density of image, and (*b*) the relation between plate sensitivity and wavelength of the incident light. Density measurements are obtained by a simply constructed selenium cell microphotometer, with which the density contour of each line can be investigated if necessary. Both visual and thermopile microphotometers are also described, and a list of papers dealing with the subject is given.

Introduction.

THIS investigation, which is preliminary to an inquiry into the distribution of intensity in the band spectrum of helium, was undertaken with the object of ascertaining the most convenient method for the purpose. In view of the increasing importance of intensities, it is desirable that, so far as technique is concerned, every possibility should be considered. Especially is it thought that any apparatus or method evolved with simplicity of construction as the end in view will be of service to others to whom the elaborate and expensive recording densitometers are not available.

It may be stated here that no attempt has been made to dispense with photography in an endeavour to gain directness ; the conditions in a discharge tube may vary so considerably in the time taken to examine directly only a few lines that at present it seems that the use of photography is unavoidable. Moreover, it is only in exceptional cases that discharges can be obtained of sufficient intensity to permit of direct investigation by means of the thermopile. Owing to the variation with wavelength of the sensitivity of plates, it follows that each one used must be standardised with a source of known spectral energy distribution.

The devices tried here arrange themselves naturally into two groups—in the first the length of the line image, which is dense at one end and fades away towards the other (the result of a progressive decrease of exposure), is taken as a measure of intensity, whilst in the second the spectrum is photographed in the usual manner, and the densities of the line images are translated into intensities by means of " density marks " on each plate. For convenience of exposition the neutral wedge apparatus is given first since its principles apply generally to the first group.

Wedge Method A.

Of the two methods of using the Hurter-Driffield Swarzschild expression [1] for the comparison of intensities, that in which the exposure time is kept constant is, on the whole, to be preferred, since in that case not only are the experimental conditions simpler, but any variations with time of the intensity of the source have no effect. Since the exposure time remains constant, it is, of course, the intensity which must be varied, and one of the simplest means of achieving this is presented by the neutral wedge placed immediately before the collimator slit. A very complete description of the use of such a wedge will be found in a series of papers by Merton and Nicholson, [2] on which the following abridged account is based.

Consider light of wavelength λ and intensity J_λ incident upon the wedge. If the material of the wedge has an extinction coefficient α_λ (for convenience referred to the base 10) for this wavelength, then the light which emerges at a place distant l from the thin end has an intensity J_λ' given by

$$\log J_\lambda' = \log J_\lambda - l\alpha_\lambda \tan\theta$$

where θ is the angle of the wedge. Or if, instead, we refer to the density D_λ of the wedge at the thick end (L being the thickness)

$$\log J_\lambda' = \log J_\lambda - lD_\lambda/L$$

where $D_\lambda = \log\left(\frac{\text{incident intensity}}{\text{transm. intensity}}\right)$. There will be some point at which J_λ' becomes equal to the critical intensity which is just sufficient to affect the photographic plate. At the point on the plate corresponding to this point on the wedge the line image will end. By measuring the length of this image and dividing it by the magnification of the spectrograph, it is possible to find the point on the wedge at which the critical intensity is being transmitted. Suppose the distance from the thin end of the wedge is l_λ. Then if ${}_cJ_\lambda'$ represents the critical intensity, we have

$$\log {}_cJ_\lambda' = \log J_\lambda - l_\lambda D_\lambda/L$$

and

$$\log J_\lambda = \log_e {}_cJ_\lambda' + l_\lambda D_\lambda/L$$

The quantity $l_\lambda D_\lambda/L$ is the logarithm to base 10 of a quantity defined in Merton's Paper as the "photographic intensity" [3] of the light λ. In order to be able to allow for the variation of sensitivity of the plate, it is necessary to use black-body radiation. For such radiation, if the temperature of the black-body be known, it is possible to calculate the values of J_λ in arbitrary units, taking as unity, for example, that at some convenient wavelength such as λ 4000 Å. To obtain the actual distribution in the light falling on the photographic plate these values have then to be corrected for the variation of the dispersion of the spectrograph. Having then photographed the black-body (with the same exposure time [4] and on the same plate as the line spectrum), we can measure the photographic intensities for a range of wavelengths. It follows, then, that for a wavelength λ

$${}_cJ_\lambda' = \left(\frac{\text{Calc. int. of black-body at } \lambda}{\text{Phot. int. of black-body at } \lambda}\right)$$

If now in the line spectrum a line of wavelength λ_1 is found to have a photographic intensity equal to X, then in order to obtain a true intensity from this (relative, of

course, to that of the black-body at λ 4000 Å.) it is necessary to multiply X by the factor

$$\left(\frac{\text{Calc. int. of black-body at } \lambda_1}{\text{Phot. int. of black-body at } \lambda_1}\right)$$

A separate experiment is necessary to determine the values of D_λ. By means of Nicol prisms, two exposures of equal duration are given, the intensity in one case being cut down to one-tenth of that in the other by suitably orientating the prisms. If in one case the point on the wedge which is transmitting the critical intensity is distant l_λ' from the thin end, whilst in the other it is distant l_λ'' then

$$\log J_\lambda = \log_e J_\lambda' + l_\lambda' D_\lambda / L$$

$$\log (J_\lambda/10) = \log_e J_\lambda' + l_\lambda'' D_\lambda / L$$

or

$$D_\lambda = L/(l_\lambda' - l_\lambda'')$$

It is to be noted that both in the determination of D_λ and in the use of the wedge any absorption in the spectrograph is eliminated.

A wedge 7 mm. long, with a density ranging from approximately 0·2 to 4·2, was obtained, and with it a photograph of the helium band at λ 4650 Å. was taken. This band is probably the strongest in this spectrum, and so offers special advantages. Upon endeavouring to measure this photograph difficulties were at once encountered. In the first place, the wedge was too dense and called for rather long exposure times. The most serious difficulty, however, was a consequence of the fact that the ends of the lines were not well defined, and large errors of measurement were unavoidable. This can be remedied by increasing the density gradient of the wedge, but, unfortunately, not only does this prevent examination of weak lines, but at the same time the sensitiveness of the method is decreased. Two alternative methods of overcoming this difficulty which have been suggested by Merton are :—

(1) Enlargement through a process screen of a positive prepared from the original negative. The screen breaks the image up into dots, and it is easier to decide upon the last visible dot than upon the actual end of the line. This method has the disadvantage of introducing two extra photographic processes and a process screen.

(2) " Cutting " the negative with a solution of potassium ferricyanide, which removes chemical fog. This is a questionable cure, since there is always the possibility of non-uniform action of the solution on the plate.

From the plates which were obtained it was difficult to obtain consistent measurements even though resort was had to the ferricyanide treatment. Some representative results are given in Table No. 1. It seems probable that the method

TABLE I.—*Some measurements obtained using the neutral wedge method.*

Two separate measurements (A and B) of the same plate gave :—

Line No.	1	2	3	4	5	6
A	33	28	64	72	71	93
B	33	38	45	70	68	74

A wedge density of 4·2 was assumed in calculating these intensities.

is of most use for quite strong lines in the visible part of the spectrum; undoubtedly in such cases, giving due consideration to the simplicity both of

construction and fundamental idea of the auxiliary apparatus required, the method leaves little to be desired. Unfortunately the construction of a wedge suitable for use in the ultra-violet presents some difficulty.[5]

Wedge Method B.

This method was suggested during work with a Fabry-Perot étalon, in which the étalon had several times been used with the plates not parallel in order to separate the emergent beams in a plane parallel to the slit. If a short collimator slit is used with the étalon in this condition the appearance in the field of view of the observing telescope is somewhat modified in that all line images are bright at one end, and fade away towards the other. In this case of course the fading is discontinuous, the image consisting of a number of rectangles of decreasing intensity placed one above the other. Now suppose that light of wavelength λ and intensity J_λ is incident upon the étalon. The series of images for this wavelength have intensities proportional to

$$J_\lambda P_\lambda^2,\ J_\lambda P_\lambda^2 R_\lambda^2,\ J_\lambda P_\lambda^2 R_\lambda^4\ \ldots,$$

where P_λ and R_λ are respectively the transmission and reflecting powers of one of the étalon films. If there are n of these images visible on the photographic plate it follows, since the intensity of the last visible image is the critical intensity for the wavelength λ, that

$${}_cJ_\lambda' = J_\lambda P_\lambda^2 R_\lambda^{2(n-1)},$$ using the notation of (A)

or $$J_\lambda = ({}_cJ_\lambda'/P_\lambda^2) R_\lambda^{2(1-n)}.$$

Comparison with the case of the neutral wedge shows that the "photographic intensity" in this case is $R_\lambda^{2(1-n)}$. Proceeding as before to standardise each plate with black-body radiation gives the factor

$$({}_cJ_\lambda'/P_\lambda^2) = \left(\frac{\text{Calc. int. for black-body at } \lambda}{\text{Phot. int. for black-body at } \lambda}\right)$$

and this may be evaluated over the whole range for which the plate is sensitive. Conversion from photographic to true intensities in the line spectrum then follows from the preceding section. To obtain the values of R_λ a separate experiment, analogous to that for the determination of D_λ of the preceding section, is required. Consider only a single wavelength and give two exposures of equal duration, one with intensity J_λ and, by means of suitably adjusted Nicol prisms, one with intensity $\frac{1}{2}J_\lambda$. If there are p images visible in the first case and q in the second, then

$$J_\lambda = ({}_cJ_\lambda'/P_\lambda^2) R_\lambda^{2(1-p)};$$
$$\tfrac{1}{2}J_\lambda = ({}_cJ_\lambda'/P_\lambda^2) R_\lambda^{2(1-q)};$$
$$\log R_\lambda = (\log \tfrac{1}{2})/2(p-q).$$

A somewhat easier though less satisfactory procedure would give two exposures of, say, $32t$ and t seconds respectively. If the first gives p and the second q visible images on the plate then, assuming that the reciprocity law[6] holds, there results

$$\log R_\lambda = \{0{\cdot}85 \log (1/32)\}/2(p-q).$$

It is admitted that this method possesses disadvantages. For example, it is possible that the last visible image for one line may be a little denser than the corresponding images for other lines. Without making measurements of density it is

not possible to make accurate allowance for this, but probably the addition of one-half to the number of images would go far to compensate for it. On the other hand, the discontinuous decrease of intensity is not entirely a disadvantage, since in the case of a continuous decrease it is a difficult matter to decide upon the end of a line. A serious disadvantage of the scheme is the inflexibility which results from its dependence on the value of the reflecting power of the metal films. Although a low value of the reflecting power such as would be obtained by using thin films gives a more rapid decrease of intensity in the series of emergent beams, thus enabling the last visible image to be more easily decided upon, yet a lengthy exposure is necessary if two lines of nearly equal intensity are under examination, for most of the light is concentrated in the first few images. Any increase of reflecting power, giving a more gradual decrease of intensity in the emergent beams, implies thickening the films. The absorption losses will now be serious and the exposure time is again lengthened.

The one great advantage of the method lies in the simplicity of the apparatus required, and although when put to the test, it failed because films thin enough to allow of photography of the band lines with a reasonable exposure time had not enough reflecting power to make the method an accurate one, it is possible that it may prove of some use as a check method for strong lines which in the most favourable cases would be separated by only a few Ångstrom units. With quartz plates and platinum films the method permits of easy extension to investigations in the ultra-violet.

Wedge Method C.

The devices described here are attempts to make use of the Swarzschild relation by varying the exposure time instead of the intensity. The appearance of the photographic image is exactly similar to that obtained with the neutral wedge. The first apparatus took the form of a toothed wheel which, when rotated before the slit of the collimator, varied the exposure time from a maximum at one end of the slit to zero at the other. Calculation showed that with a wheel 8 cm. in diameter and with some ten or more teeth it could be assumed that the exposure time when so varied increased linearly. This method proved to have a serious defect in that the discharge producing the band spectrum was of a semi-periodic nature, and it was not possible to prevent the rotating wheel from showing some sort of stroboscopic effect, which at once nullified its occulting action. The device was, therefore, modified, and finally took the form of a cam-driven shutter moving vertically before the slit. The motive power for the cam, which was designed to drive the shutter with constant velocity, was supplied by an electric motor geared down so that the final speed was about three revolutions per minute. Two or three satisfactory photographs were obtained. When an attempt to measure these was made, however, considerable difficulty was experienced in determining the positions of the ends of the lines, and records of the same plate differed so widely that it was clear that it was not worth while to spend time in elaborating the method. Some specimen measurements are given in Table No. II.

Table II.—*Some measurements obtained by varying the time of exposure along the slit.*

Line No.	1	2	3	4	5	6
A	100	100	65	48	31	11
B	80	100	55	40	25	8

Densitometer Methods.

In the methods which had so far been tried the difficulty of estimating the end of the line was always a source of inaccuracy, although considerable practice might have trained the eye and improved the consistency of the results. In the light of the experience which had been gained it seemed that a more profitable approach would be by measuring the density of lines in a spectrogram taken in the usual way; intensities could then be obtained from a density scale photographed on the same plate. The first part of the problem is one for microphotometry. The advantage of selenium in work of this kind is well known—its great sensitivity to light permitting of the construction of sensitive cells of very small size. Again, there is not with selenium that need for protection against the stray thermal radiation which is so troublesome a source of disturbance with the thermopile, nor does one require any auxiliary amplifying devices, as is the case with the photoelectric cell. The objectionable properties of selenium are well known. In spite of these it was decided to make use of a selenium cell.

First (Selenium Cell) Densitometer Method.

The photographic plate to be examined was placed in a carrier which could be traversed by means of a micrometer screw (one division on the divided head corresponded to a movement of 0·01 mm.) to and fro between the condensing and projection lenses. The latter was a Taylor-Hobson camera lens of focal length 115 mm. ($f/4{\cdot}5$), giving a twenty-five times magnified image at a distance of about 3 metres. A hundred candle-power half-watt lamp was used for a light source. The linear selenium cell, designed by Professor Thirring, consists of a narrow strip of selenium mounted between two brass blocks upon which the terminals are mounted. The dimensions of the active selenium surface (which is protected by a thin transparent plate) are 11 mm. by 0·17 mm.

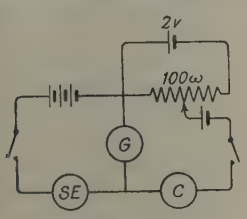


Diagram 1.

The literature of the subject indicated that a procedure advocated by Fournier d'Albe[7] had met with some success. The cell was to be made part of a battery bridge; alternately illuminating and darkening the cell for equal periods of time then caused the galvanometer spot to travel to and fro over the scale, and when after a short time the amplitude of this became constant it was taken as a measure of the intensity of the incident light. In order to make certain that the alternations were regularly performed, a revolving shutter was constructed of three 60° sectors, and fitted to the spindle of a stop-clock. This shutter was placed immediately before the cell, and in this way periods of ten seconds light and darkness were automatically obtained. The circuit employed with the selenium cell is shown in Diagram No. 1. The cell *SE* had a dark resistance of the order of 20 megohms, and was balanced by the graphite line resistance *C*, value 1 megohm. The galvanometer *G* was of the Onwood moving coil pattern, with a resistance of 1053 ohms and a sensitivity of about 10^{-8} amps. per mm. at 1 metre. Usually in such a circuit as this a galvanometer of much higher resistance would be employed; but since in this particular case it was found that ample sensitivity had been obtained, the Onwood galvanometer (unless otherwise stated) was used throughout. Some trials were

first made with a modification of the method; the cell was kept dark most of the time, and illumination was confined to periods of only 1/50 sec., the resulting kick of the ballistic galvanometer being taken as a measure of the light intensity. The results were not good, but it is possible that they could have been improved by the use of a more accurate shutter. A test was next made of the relation (which according to Fournier d'Albe is linear) between light intensity and amplitude of galvanometer swing. A knowledge of this relation is not necessary to the working of the method if density marks are on each plate; but unless it is known, however, it is not possible to obtain the actual densities of the various parts of the plate. A small pea-lamp was placed at various distances from the cell, and the corresponding amplitude for each position of the lamp obtained. These amplitudes were then plotted against arbitrary units of intensity. The curve was not linear, but showed a decrease in slope for increasing intensities, as shown in Diagram No. 2. It was thought that this might be due to reflected light reaching the cell; but, although careful screening removed all possibility of this, the shape of the curve remained the same. For this reason it was not possible, with this method, to convert easily plate readings into densities. This result will not be discussed further, for it seems that it is usual with commercial selenium cells containing metallic selenium. [8] The next step was to make measurements on some band-lines, of which several plates had been obtained on the Hilger constant deviation spectrometer. These lines were at this stage of the work not directly the subject of the investigation; two of the best plates, therefore, were chosen, and attention was confined mainly to these in an endeavour to obtain constant results. The two chosen plates came respectively from batches of the Ilford Panchromatic and Empress brands. The procedure adopted with these plates was as follows:—

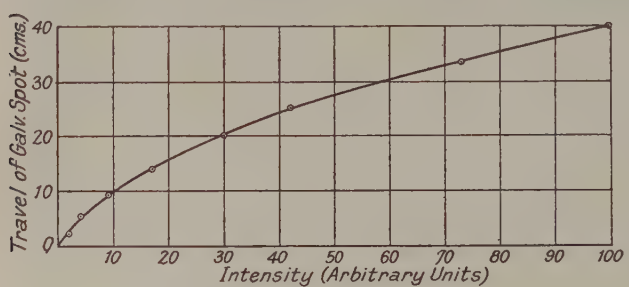


DIAGRAM 2.

Measurements were first made on the density marks (five in number), when the plate was removed and replaced so that the band-lines, some twenty in number, were projected on the plane of the cell, care being taken to see that the plate was so orientated that the cell came truly down the middle of each line. The plate was then moved along so that each line in turn fell on the cell, observation of the galvanometer spot (without the shutter rotating) showing when the cell was covered by the densest part of the line. Then the shutter was started, and usually after five or six alternations of intensity the amplitude of swing of the galvanometer spot became constant. At the end of a run the motion of the plate was reversed, and some of the first measurements repeated to make sure that the constants of the cell were unaltered. The measurements of the density marks provided material for the construction of an intensity calibration curve, from which, by interpolation, the intensities of the band-lines, in arbitrary units, could be obtained. The process

is somewhat lengthy, but the results (of which specimens are given in Table No. III) both in consistency and accuracy were vastly superior to any that had been obtained previously. It was during these measurements that a fatigue effect was noticed

TABLE III.—*Some measurements obtained using the selenium cell as a photometer.*

Patch No.	1	2	3	4	5
A (March 4), mm.	126	96	54	35	29
B (March 6), mm.	127	98	55	37	30

The readings are the amplitudes of the swing of the galvanometer spot.

Line No.	1	2	3	4	5	*6	*7	*8
Intensity in Arbitrary Units.								
A (Jan. 5)	30	42	47	43	37	31	28	18
B (Feb. 13)	30	43	48	45	39	35	25	16

Both *A* and *B* were obtained from the same plate, measured on the dates given at the head of the columns.

when the cell was subjected to constant intense illumination, and some special experiments were made to ascertain the nature of this phenomenon. The cell was placed at a distance of about twelve inches from a small lamp which, with an ammeter, was supplied with current from an accumulator. The voltage was applied to the selenium cell, and the bridge was balanced about an hour before the test was made. The position of the galvanometer spot was quite constant during this period. The lamp circuit was then made, and readings of both the ammeter and bridge galvanometer were taken over a period of some hours. The existence of the fatigue was clearly demonstrated. In order to see to what extent the fatigue might be modified by previous treatment (with the object of fully fatiguing the cell before use) some separate experiments were made. These showed that much of the effect could be removed by a previous strong illumination, although to a slight extent it was always in evidence.

A little difficulty was experienced with the varying opacity of the unexposed parts of the panchromatic plates, and it seems that it is this fault which will probably limit the accuracy of photographic methods. This necessitated the measurement of a number of unexposed parts of the plate and the adoption of a mean value. One source of error was found to arise from imperfect focussing of the lines on the cell. If the focussing was not attended to so that the best conditions prevailed the results were not consistent. The method, in view of the results obtained, is clearly a practicable one, and its only disadvantage lies in the fact that it is somewhat lengthy. Nevertheless, it was thought that existing knowledge of the properties of selenium pointed to the fact that it was better to use it as a judge of equality of illumination rather than directly to make its change of resistance a measure of the intensity of illumination. It was consequent upon this decision that a modification of the device used by Toy was constructed.

* These lines are not fully exposed. In such cases as this the more horizontal part of the density-intensity curve of the photographic plate is being used, so that any errors in setting the line on the cell, or any irregularities in the film, are here relatively more important.

SECOND (SELENIUM CELL) DENSITOMETER METHOD.

The apparatus was arranged as shown in the accompanying Diagram No. 3. The selenium cell *A* and plate and projection system *B* are identical with those of the last method. At *C*, however, is a device for projecting an illuminated patch on the cell. The intensity of this patch can be regulated at will by sliding the shutter 1, which carries a scale moving over a pointer, before the slit in the screen 2. The selenium cell and the ground glass 3 are at conjugate points of the cylindrical lens 4. The illuminating lamp *C* is of the same size and type as that in the projection system and the two are so connected that by means of a switch it is possible to change over very rapidly from one to the other. A future apparatus would be constructed on a much smaller scale and in this case two shutter-controlled beams from the same lamp (instead of two separately controlled lamps) would be installed. It was not practicable to use only one lamp with the existing apparatus and in use the two lamps caused no difficulty.

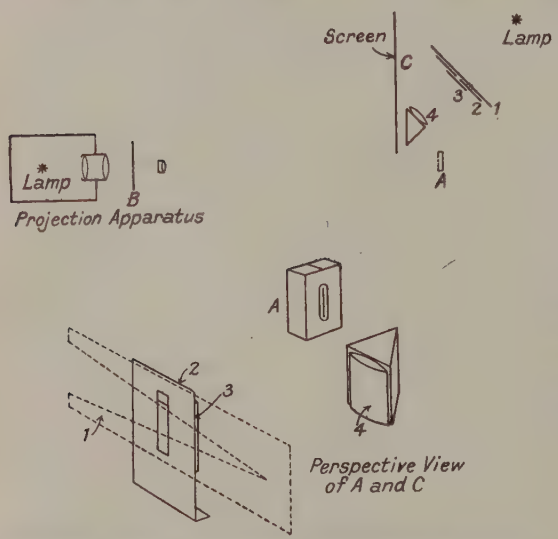


DIAGRAM 3.—ARRANGEMENT OF APPARATUS IN SELENIUM CELL PHOTOMETER.

The procedure adopted when measuring was similar to that of the preceding method; the plate was moved along until the image of the line under examination fell upon the cell, when further slight adjustments were required until the galvanometer showed that the cell was correctly placed in the densest part of the image. The shutter 1 was then placed in such a position that upon changing over rapidly from one lamp to the other no movement of the galvanometer spot occurred. When this condition is satisfied it is evident that the intensity of the shutter-controlled patch (of which the reading on the scale attached to the shutter 1 is a measure) has the same value as that of the portion of the image of the plate which falls on the cell. It was arranged that the minimum scale reading corresponded to that position of the shutter in which no light reached the cell, whilst the maximum reading (by suitably adjusting the position of the lamp at *C*) gave about the same illumination on the cell as the clear part of the plate under examination.

The method was simple of operation and comparatively rapid whilst in sensitiveness and accuracy it left nothing to be desired.

The only fault was its inability to become self-recording. As with the previous method some care was necessary when focussing otherwise consistent results were not obtained. However, it was remarked that, of two consecutive runs of the same

plate, although the actual intensities on the arbitrary scale were not exactly the same, yet when reduced to terms of the strongest line a good agreement was obtained. Some typical results obtained with this method are shown in Table No. IV.

TABLE IV.—*Some measurements made with a Toy and Rawling type densitometer.*

Patch No.	1	2	3	4	5	6
A (March 27, 1926) ...	78	54	23	11	8	6
B (Jan. 6, 1927) ...	80	52	22	10	8	6

The figures are the readings on the densitometer scale.

Line No.	1	2	3	4	5	6	7	*8
Intensity in Arbitrary Units.								
March 27, 1926	32	45	51	47	42	37	28	18
Jan. 6, 1927	34	44	49	46	42	37	28	22

The apparatus, too, has further possibilities in that with it the density contour of a line may be obtained, from which in some cases the presence of an unresolved component might be inferred. For example, with the Hilger constant deviation spectrometer which as here adjusted was just able to resolve $Q1$ and $Q2$ of the He 4650 band, an interval of 0·9 Å.U., the lines $P4$ and $Q9$ (being separated by only 0·5 Å.U.) were not resolved. On obtaining the contour of the line $P4$, which to visual examination was single, the presence of another line was at once apparent. A control experiment on $P5$ showed that the contour for this line was quite symmetrical (*see* Diagram No. 4). Since the width of a line image when projected on the cell is about 1·5 mm., whilst that of the cell is only 0·17 mm., the reason for this sensitiveness is obvious. The superior sensitivity of selenium which permits of the construction of so small a detector is, of course, a contributory factor. It will be seen that the resolving power of this densitometer was quite sufficient for the spectrograms which were used. In order to be quite certain that these selenium cell densitometers were giving correct indications a model of the more usual thermopile type was constructed. A short description of this is included here.

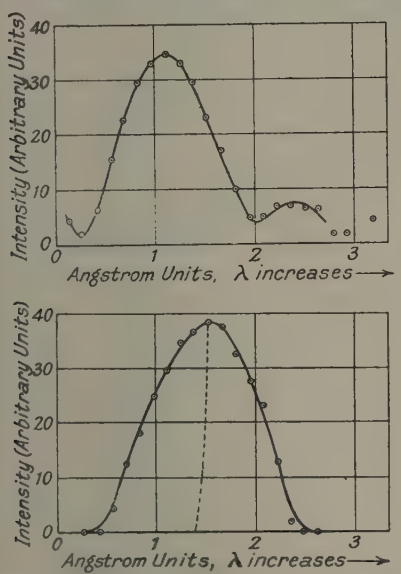


DIAGRAM 4.—THE CALCULATED RESOLVING POWER OF THE SPECTROMETER, FOR ZERO SLIT WIDTH, IS 8606. THIS CORRESPONDS TO AN INTERVAL OF 0·55Å.U.
The upper curve refers to *P5*.

* This line is underexposed.

THIRD (THERMOPILE) DENSITOMETER METHOD.

In accordance with the general aim of this work the construction was simplified as much as possible. Much of the detail can be gathered from Diagram No. 5. The 100 candle-power half-watt lamp *A* is turned so that its semicircular filament lies in the vertical plane which contains the optic axis of the system. When in this position a very intense image (approximately linear) can be obtained on the slit *B* which is 0·04 mm. wide and about 10 mm. long. This slit can very conveniently be constructed of razor blades of the paper-steel type clamped in a holder similar to that shown. The slit now acts as source for the microscope objective *C*, 3 cms. focal length, which projects a reduced image of the slit on to the photographic plate *D*. The plate is carried in a traversing holder. The lens *E* is used to image the illuminated portion of the plate on the thermopile *F*, which with its brass mounting was taken from a Hilger infra-red spectrometer. The resistance of the thermopile was 8·6 ohms. The galvanometer was of the Broca type and had a resistance of about 12 ohms; the sensitivity when in use was of the order of 10^{-10} amp., but owing to a heavy magnet system the period at this sensitivity was rather long. Three concentric iron shields provided adequate magnetic screening. A cardboard tube lagged with cotton wool placed about the thermopile prevented disturbances due to draughts, but unfortunately this was not able to stop a slow drift of the galvanometer spot due presumably to radiation from the observer. It was finally necessary to make the instrument self-recording. This was done with the aid of a small motor, which drove the micrometer screw of the plate holder through a reduction gear, and a recording camera. Upon examining the records obtained with this apparatus it was found that, so far as the density marks were concerned, there was no reason to suspect those obtained by the preceding method. With the lines the agreement is bad, and from the photographic trace it is clear that this must be due to lack of resolving power of this densitometer. It is a difficult matter to limit the illuminated area on the plate to a strip smaller than a spectral line, and yet to pass enough energy to enable the galvanometer to be used with a moderate sensitivity. As a check on the measurements a plate was sent to Messrs. Adam Hilger for examination on their Moll densitometer. Unfortunately, only the low resolving power apparatus was available and the trace from this showed the same characteristics as the one already obtained—good agreement for the density marks but poor agreement for the lines. It is a surprising circumstance, however, that the intensities, when given in terms of that of the strongest line, have values in fair agreement with the rest. (*See* Table V.)

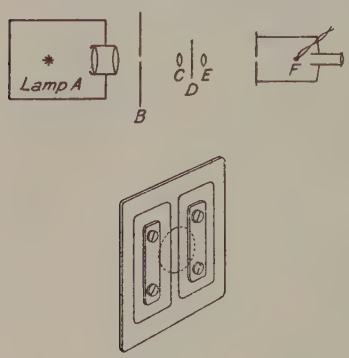


DIAGRAM 5.

It was now that, through the kindness of Professor L. C. Martin, of the Royal College of Science, an opportunity was obtained to use an optical densitometer.

TABLE V.—*Results obtained from the thermopile densitometers, compared with some obtained with a selenium cell.*

Line.	Moll. inst. A.	Lab. inst. B.	Se. cell. C.	A′.	B′.	C′.
Q3	42	60	71	100	100	100
4	37	54	65	88	90	92
5	31	45	58	74	75	82
6	29	39	48	69	65	68
7	18	23	29	43	38	41
P3	30	38	51	72	63	72
4	29	38	50	69	63	70
5	27	36	40	64	58	56
6	19	24	29	45	40	41
R1	35	48	59	83	80	83
2	33	47	57	79	78	80
3	30	43	54	71	72	76
4	26	38	47	62	63	66
5	22	30	35	52	50	49

The values A, B, C should be identical.

The column A′ is obtained by multiplying the values of column A by a factor which makes the intensity of Q3=100. The values B′ and C′ are derived similarly.

FOURTH (OPTICAL) DENSITOMETER METHOD.

For a complete account of the principle and construction of this apparatus reference should be made to Trans. Opt. Soc., 26 (1924-25), 109. Briefly, however, the apparatus (shown in Diagram No. 6) consists of a microscope containing a Lummer Brodhun prism, which divides the field of view into two parts. The central part of the field is occupied by the portion of the plate under examination illuminated by the beam which travels via condenser, reflecting prism, diaphragm and opal glass No. 1. The outer portion of the field is illuminated by the beam which comes via the neutral tinted wedge and opal No. 2. The neutral wedge is moved to and fro until both parts of the field are judged to be of equal intensity. The scale reading of the pointer attached to the wedge is then taken as a measure of the intensity, or if the wedge has previously been calibrated, the actual density of the image on the plate can be obtained. The apparatus, which was more or less an experimental model, proved quite sensitive, and the intensity values obtained with it agreed well with those obtained by other methods. Some specimen results are given in the adjoining Table No. VI. It was noticed, however, that measurement of more than a few lines was a little tiring, and with fatigued sight the accuracy fell rapidly. It is also somewhat difficult to match the two parts of the field if the tint of the wedge is not the same as that of the exposed plate.

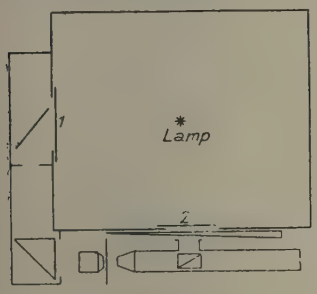


DIAGRAM 6.

TABLE VI.

Line	Q1.	Q2.	Q3.	Q4.	Q5.	Q6.	Q7.
Densitometer Reading, July 12 ...	124	110	106	110	120	131	137
„ „ July 14 ...	122	109	106	111	119	129	135

The readings are of the scale over which the neutral wedge moves.

Conversion from Microphotometer Readings to Intensities.

The Calibration Marks.

These marks were obtained by means of a stepped aperture, which was illuminated by a tungsten filament lamp, and a cylindrical lens. In this way there were projected on to the slit of the spectroscope five images (of continuous spectra) of progressively increasing density.

The intensity scale was examined in the following manner. Two sets, say, A and B, of intensity marks were obtained on a plate, the intensities in set A being 4/3 those in set B. This was done approximately by varying the width of the spectrometer slit. The densities of each set of images were then measured and plotted against the intensity-mark number, and in each case a smooth curve drawn through the points so obtained. It is now necessary to search for points in A and B which have the same density. Suppose marks Nos. 1 and 1·5 in set A have the same densities as those of 1·5 and 2 respectively in set B. From this information it is deduced that intensity-mark 1·5 has 4/3 the intensity of mark 1, and that mark 2 has 4/3 the intensity of mark 1·5. Proceeding in this manner the relative intensities over the whole scale can be determined. The result of such an investigation for one of the apertures which was used is shown in Diagram No. 7.

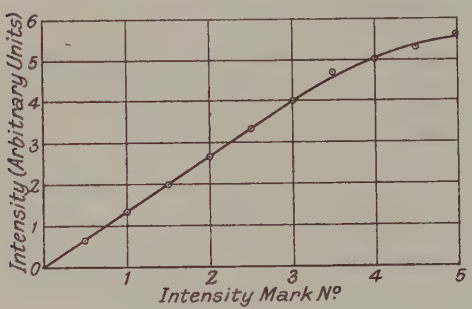


Diagram 7.

The Change in Plate Sensitivity.

Since the photographic plate is not equally sensitive to all parts of the spectrum a further calibration is necessary, especially when the range of the line spectrum under examination is large, or when the lines fall in a region in which the sensitivity of the plate varies rapidly. It must be remembered too, that selective absorption will occur in the spectroscope, but this can be included in and determined with the characteristics of the plate. The method by which these characteristics are usually determined consists of photographing a source of known spectral energy distribution, and evaluating its distribution, neglecting the peculiarities of the plate. Comparison of the measured with the known distribution then enables a correction factor for each wavelength to be determined. The most convenient source is a black-body, and both the positive crater of the carbon arc and hollow tungsten filaments have been employed in this capacity. Much information on this point may be gathered from reference No. 37. An estimation of the sensitivity variation may also be made by making use of the fact that within the visible spectrum the energy distribution of a tungsten filament lamp is approximately that of a black-body at some slightly higher temperature known as the "colour temperature." The relation between true and colour temperatures is given in reference No. 37. The true temperature of the filament may be determined from its change of resistsance with temperature, or

by means of a pyrometer. At high temperatures a sufficiently approximate formula for the calculation of the distribution is

$$J_\lambda \propto \lambda^{-5} e^{-a/\lambda T},$$

where $a = 1{\cdot}445$ cm. degree. If a prism spectrograph is used the dispersion of the prism must also be taken into account.

The Conversion to Intensities.

To illustrate the final steps of the work, some measurements of the λ 4650 helium band obtained with a Toy and Rawlings' type densitometer, are given in Table VII. From the calibration marks a curve is drawn connecting densitometer

TABLE VII.—*Measurements on* λ 4650 *helium band.*

Intensity	0	20	40	60
Densitometer Reading	80	52	22	10

Line.	Densitometer Reading.	Intensity.
Q 1	30	34
2	18	44
3	14	49
4	16	46
5	20	42
6	26	37
7	40	28
R 1	30	34
2	31	33
3	30	34
4	33	32
5	38	29
P 2	52	20
3	32	33
4	28	36
5	35	31
6	46	24
7	58	17

reading with intensity. The relative intensities of the spectral lines are then obtained by interpolation on this curve. It should be added that, under the circumstances in which the plate was obtained, there was no correction for change of sensitivity.

Comparison of Results.

A survey of the results gained by means of the methods previously described leads to the following estimates of the probable errors to be expected: Method A, probable error, 25 to 30 per cent.; method C, 10 per cent. First and second densitometer methods, densities 2 per cent., intensities 5 to 7 per cent. Fourth densitometer method, 7 per cent.

CONCLUSION.

From the results which have been obtained so far the following conclusions may be drawn. Firstly, that although these methods of which the neutral wedge is typical may be very useful with strong lines, with weaker lines such as are found

in the helium bands it is better to photograph the lines in the usual way and endeavour to interpret intensities from densities. Secondly, that although it is not impossible to obtain density measures directly from the indications of the selenium cell, it is far better used, both as regards convenience and sensitiveness, in a secondary position merely as a detector of equality of illumination. And lastly, that although the method due to Toy may suffer from the disadvantage that it cannot easily be made self-recording, yet in sensitiveness and reliability it gives greater advantages than any other which has so far been tried.

In conclusion, the writer wishes to express his indebtedness to Professor W. E. Curtis, by whom the problem was suggested, for advice and criticism throughout the work.

References.

(1) This expression states that density of photographic image $=\gamma \log (J t^{p/i})$, where γ, p, i are constants, J represents intensity and t time.

(2) Phil. Trans., 216, p. 459; 217, p. 237; 220, p. 137.

(3) Since if we assume that ${}_cJ_\lambda'$ is independent of λ, which amounts to the same thing as neglecting the variation of the light-sensitivity of the plate, the quantity $10^{k_\lambda D_\lambda / L}$ is a measure of J_λ.

(4) If this is not adhered to it may happen, if the index in $J.t^p$ is a function of λ as it sometimes is, that the values of ${}_cJ_\lambda'$ calculated from the black-body cannot truly be applied to the line spectrum.

(5) T. R. Merton. Proc. Roy. Soc., 106 (1924), 378.

(6) For constant density $J_\lambda . t^p = \text{const}$, where $p \simeq .85$.

(7) Proc. Roy. Soc., A. 89 (1913), 75.

(8) Gudden and Pohl. Zeits. f. Phys., 35 (1925), 243.

(9) Proc. Phys. Soc., 36 (1924), 432.

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DISCUSSION.

Mr. J. O. C. VICK asked the Author whether he had tried the method of sharpening the end of the line image obtained with the wedge which consists in contact-printing from the original negative, and again printing if necessary from the copy, the process being repeated as often as may be required. In using the Toy and Rawlings densitometer, how had he controlled the cross-section of the two light pencils to be compared? He might find useful the new design

of this apparatus, which employs a photo-electric cell associated with a valve amplifier, and is adapted to the photometry of fairly broad spectral lines.

The AUTHOR replied that he thought that repeated contact printing would destroy the sensitiveness of the wedge method as applied to investigations on spectral lines. As to the new apparatus, he thought that it was a great advance on Dr. Toy's earlier model.

Dr. L. C. MARTIN: I should like to thank Mr. Childs for his interesting and useful Paper. Has he made any attempt to apply the wire-grating method of obtaining spectra of known relative intensities? Also, I should like to know how much value he attaches to the density contours of spectrum lines which can be obtained with densitometers at present available. The correction for finite width of slits is often likely to mask the true density, and with the photographic plates available it is very difficult to obtain results which are not seriously affected by the size of the grain. Trials of photographs of lines with known relative intensities have not always been very encouraging, especially with recording instruments.

AUTHOR'S reply to Dr. Martin: Dr. Martin raises several interesting and important questions. I have not tried the wire-grating method which he suggests. Although I understand that its use in astronomical investigations has met with some success, application to a problem such as that mentioned in the Paper would probably introduce difficulties into the photometry of the resultant negative, owing to the continuous change of intensity on going from one order grating image to the next. The density contours shown in the Paper are, of course, of little use from an intensity point of view, since integrating under the curves would probably be stretching the method a little too far. What was intended, however, was to demonstrate that a simple photometer, such as the one described, was capable of giving more information (as to non-symmetry) than could be gathered from visual examination. The effect of the grain of photographic plates is admittedly troublesome, especially with the fastest plates. Most microphotometers do much to mitigate the effect by integrating the transmitted light over a length of the line image. It must be remembered, too, that the effect of grain will probably be much the same in both line image and calibration mark

XVIII.—ELECTRICAL METHODS OF HYGROMETRY.

By P. W. Burbidge, *M.Sc.*, *B.A.*, Professor of Physics, and N. S. Alexander, *M.Sc.*, Auckland University College, New Zealand.

Abstract.

An account is given of experiments performed to investigate the possibility of applying electrical methods to the measurement of humidity. Two methods are considered, depending on (1) the change in resistance of organic materials (cotton-wool and human hair) on exposure to water vapour ; (2) the change in mobility of ions due to water vapour.

Results show that in the first case the change in resistance with humidity is not linear, the logarithm of resistance being proportional to the humidity, while in the second the effect produced is too small to permit of accurate measurement. Thus, in neither case does the method seem suitable for general use, though each could be applied in special cases.

OF the three types of hygrometer in general use for the measurement of atmospheric humidity—viz., the wet and dry bulb, dewpoint, and hair hygrometers—each has certain disadvantages, and none appears capable of a high degree of precision. The present investigation was undertaken with a view to determining the possibility of applying electrical methods to the measurement of atmospheric humidity. Two methods were considered, the first depending on the change in electrical resistance of organic materials on absorption of water vapour, the second on the variation in mobility of ions caused by water vapour.

I. Electrical Resistance Method.

Masson and Richards* investigated the mass of water absorbed by cotton on exposure to air of various humidities, a more detailed study of the same phenomenon being carried out later by Trouton and Miss Pool.† A considerable lag is indicated, and the relation between vapour pressure and mass absorbed appears to be parabolic, Masson later indicating an asymptotic approach to saturation values. These investigations showed that the mass of water absorbed depends on the relative humidity and not on the absolute vapour pressure.

Barr‡ describes an electrical resistance hygrometer, but abandons it on account of the large lag, which, however, appears to be due to the form of the instrument.

In the experiments now described, a layer of pure cotton-wool, of such thickness as to be semi-transparent, was placed between two electrodes in the form of a grid (Fig. 1), the whole being mounted through insulating bushings inside a metal box with a close-fitting lid.

The air in this box could be brought to any desired humidity by circulating it by means of a fan over the surface of sulphuric acid solutions of known density contained in large shallow dishes.

The resistance was measured directly by means of a high potential (100-500 volts) and galvanometer. Ohm's law was obeyed, and no polarisation effect could be observed.

* Proc. Roy. Soc. (1906).
† *Ibid.*
‡ Proc. Roy. Soc. (Feb., 1922).

The variation of resistance with humidity was found to be such that, on plotting the logarithm of resistance against vapour pressure (at constant temperature), a straight line was obtained (Fig. 2). At high humidities the resistance decreased enormously, and trustworthy readings could not be obtained above 95 per cent. humidity.

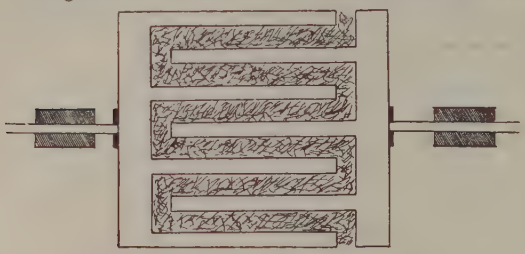


FIG. 1.—COTTON-WOOL RESISTANCE UNIT.

The lag appeared excessive, but this was attributed to the time taken for the air to come into equilibrium with the solution, so further experiments were made to eliminate this effect.

The specimen, as before, was contained in a small box which could be placed in communication with either of two larger boxes containing air at the desired humidity, the air being thoroughly mixed by means of a fan. Humidities were measured by means of a dew point hygrometer of a form due to Holtzmann,* by means of which the humidity of the air close to the specimen could be determined (Fig. 3).

The lag was found to be of the order of 5 to 6 minutes, varying with the thickness of the specimen, but fairly constant over wide ranges of humidity. A more accurate calibration of the specimen over a limited range confirmed previous observations, and showed an agreement within 2 per cent. between values obtained with rising and falling humidities.

Temperature Effects.—The relative humidity was kept constant at 70 per cent., and the temperature of the air varied by circulating it over a heating coil, the temperature

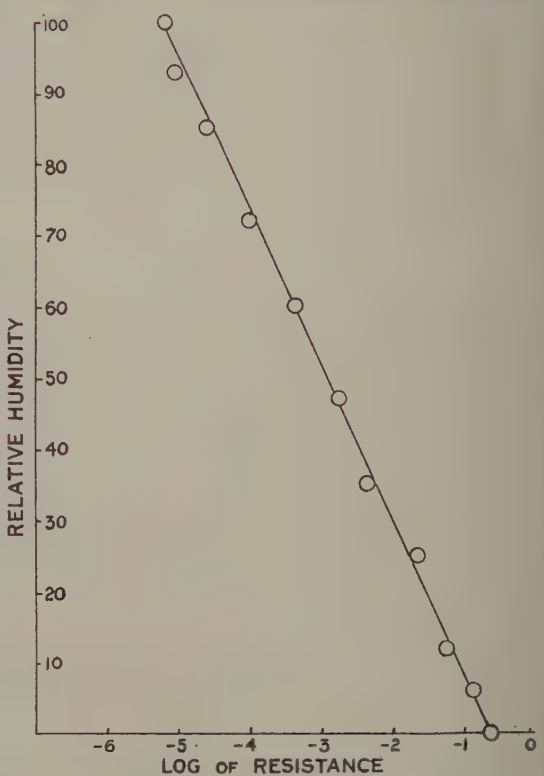


FIG. 2.—VARIATION OF RESISTANCE WITH HUMIDITY (COTTON-WOOL).

* Phys. Zeit. (Sept., 1924).

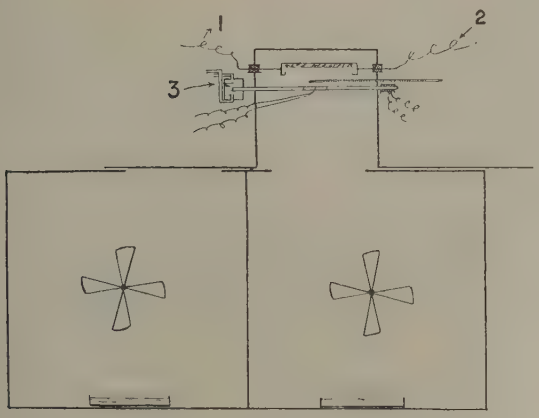


FIG. 3.—SECOND FORM OF HUMIDITY APPARATUS.

1. High potential lead. 2. Galvanometer lead. 3. Holtzmann hygrometer.

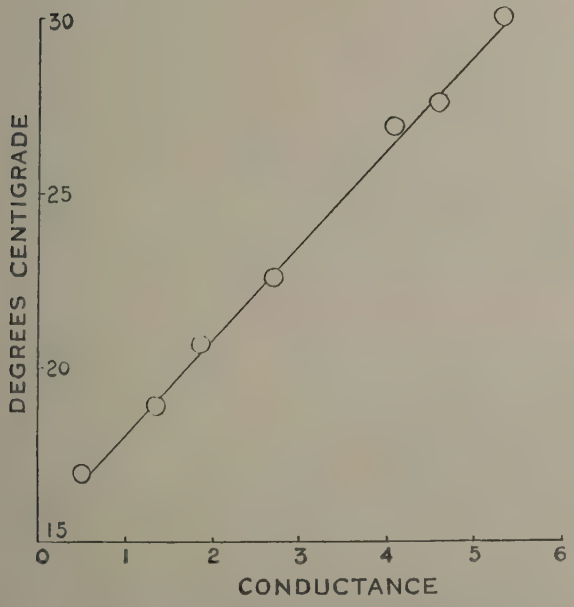


FIG. 4.—VARIATION OF CONDUCTANCE WITH TEMPERATURE (COTTON-WOOL).

being measured by means of a mercury thermometer with the bulb placed close to the specimen. A linear relation was observed between temperature and reciprocal of resistance, showing that the resistance depends more nearly on the absolute vapour pressure than on the relative humidity (Fig. 4).

The experiments were repeated with human hair freed from grease by repeated extraction with alcohol. The change in electrical resistance with humidity was found to be of a very different type from the change in length, the decrease in resistance being small from 0 to 50 per cent. humidity, but greater at high humidities (Fig. 5).

This seems to indicate that resistance and elongation are governed by separate conditions, the former probably a surface effect, the latter depending on the water-content of hair cells. In other respects its behaviour resembles that of cotton wool. Its calibration curve (log of resistance against humidity) is not linear, giving a greater proportional decrease in resistance at higher humidities. The curve obtained on plotting temperature against reciprocal of resistance is likewise not linear.

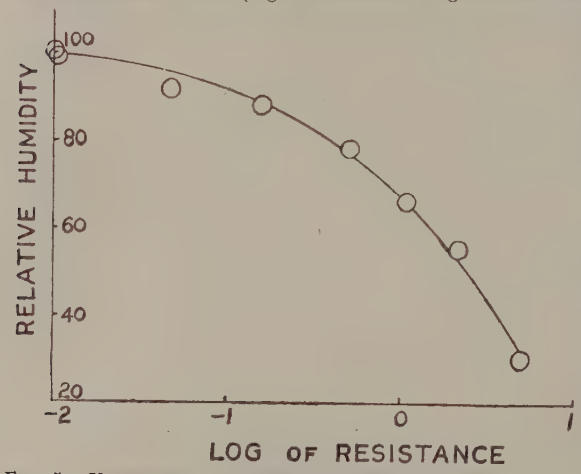


FIG. 5.—VARIATION OF RESISTANCE WITH HUMIDITY (HAIR).

The results obtained indicate that an instrument employing this principle would be insensitive at low humidities, though it could be employed over a limited range. It would also be liable to disturbance by changes in temperature, and possibly by acid or saline impurities in the air.

After the commencement of this work, an abstract was noted in Science Progress, July, 1926, of a Paper by Albrecht,* describing a similar type of instrument.

II. IONISATION METHOD.

Tyndall and Grindley† investigated the effect of moisture on the mobility of ions, the mobility of negative ions being shown to decrease from 2·15 in dry air to 1·60 at saturation. If then ionisation is produced in air subjected to an electric field less than that necessary to give saturation, the ions will remain subject to a certain amount of recombination. If the mobility is decreased, the time for recombination, and hence its amount, should also increase to an extent depending on the water vapour present. According to Tyndall and Grindley, the positive ion when first formed has a mobility indistinguishable from that of the negative ion, and similarly affected by water vapour. The positive ion is, however, rapidly transformed

* Beitrage zur Phys. der Fr. Atm., 11, 4.
† Proc. Roy. Soc. (Feb., 1926).

into a slower moving type, the rate of transformation being decreased by water vapour. Hence in damp air it has a longer period of higher mobility, and thus possibly a higher average mobility. This would tend to oppose the effect of water vapour in diminishing the current.

Experiments were carried out to determine if the change in ionisation current could be made sufficiently great to enable the method to be applied to the measurement of humidity. A hygrometer on this principle would have no lag, an approximately uniform scale, and would measure the absolute amount of water-vapour present in the air.

The apparatus consisted of an ionisation can with two electrodes, the contained air being brought to the desired humidity by acid solutions as before. Two sources of ionisation, γ-rays, from radium and α-rays from uranium oxide freed from radioactive impurities, were used. Currents were measured by determining the rate of charge of a Wilson electroscope. Saturation curves were obtained as shown (Fig. 6). These indicate that the maximum difference in ionisation current obtainable between 0 and 100 per cent. humidity is too small to permit accurate measurement, particularly as the ionisation current would be affected by impurities such as hydrogen and sulphur dioxide, and by variations in temperature and pressure.

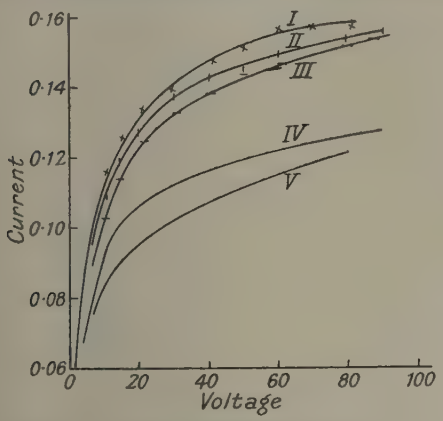


FIG. 6.—RELATION BETWEEN IONISATION AND HUMIDITY.
γ-Ray Ionisation—I Dry Air; II 56% Humidity; III Saturated Air.
α-Ray Ionisation—IV Dry Air; V Saturated Air.

In the Report of the N.P.L. for 1926, p. 64, reference is made to work on the effect of humidity on the mobility of ions. (By opposing the motion of the ions by means of a constant air-current, effects on a larger scale than above are obtained, but the application of this principle to a simple form of hygrometer would involve the difficulty of maintaining a constant flow of gas.)

III. CONCLUSION.

Since the investigation showed that such instruments would not be of great value for the measurement of humidity, no further work was done. Although suffering from various disadvantages, the instruments would appear to compare favourably with other types in use, e.g., the hair hygrometer, especially in the region of higher humidities; their time lag is small, and both forms, especially the first, could be very easily made distant-reading or recording.

DISCUSSION.

Prof. A. M. TYNDALL: The Author refers to some work done by Mr. Grindley and myself on the effect of water vapour on the mobility of positive ions. This work has recently been carried further, but the results so far obtained are of a complex character and are difficult to

interpret. In this connection I should like to ask whether the Authors are inclined to attach any significance to the difference in the shape of the two curves IV and V in Fig. 6, or whether they think that the more rapid rise of curve IV is due to accidental causes.

Dr. Ezer Griffiths: The Paper is interesting, as it illustrates some of the difficulties encountered when an attempt is made to utilise the electrical properties of a hygroscopic material in the design of a hygrometer. With a loosely packed material, such as cotton-wool, imperfect electrical contact of the material with the electrodes is inevitable, and the conduction of electricity under such conditions is complicated by many variables. It would be interesting to know how accurately the line shown in Fig. 2 can be reproduced after a period of time. The Authors state that agreement within 2 per cent. is obtained between observations on rising and falling humidities. In a Paper by F. P. Slater, published in Proceedings B of the Royal Society, 1924, data are given for the change of electrical conductivity of a single cotton fibre with variations in humidity, and it was stated that equilibrium was not obtained even after the lapse of 24 hours after making a change in the humidity. It would therefore seem that the subject merits further investigation. The Authors refer to the Report of the N.P.L. for 1926, which contains a brief reference to some work on the effect of humidity on the mobility of ions. As this work was carried out by my colleague Mr. Awbery and myself, a few remarks concerning it may be of interest, as we have not yet published a detailed account. At the time we were seeking for a method of measuring fairly rapid changes of humidity, and it was suggested that the variation of mobility of ions with humidity might constitute the basis of a method. Since the relation between humidity and mobility was not then known (the only data available, so far as we knew, being the isolated observation of Zeleny that the mobility of the negative ion in dry air was 1·24 times the mobility of that ion in moist air), our initial efforts were directed to the determination of this relation. We tried the method described by Burbidge and Alexander, but did not find it satisfactory. We employed a thin layer of uranium oxide spread over an aluminium plate and covered by layers of thin aluminium foil, the number of layers being so adjusted that the α rays just emerged and produced an ionised layer of gas close to the plate surface. Whilst there was no difficulty in measuring the small ionisation currents produced, a very formidable difficulty was encountered in the variability of the contact potential effects. With no applied voltage, a small ionisation current was obtained which varied erratically. Changes of temperature of the electrodes had a marked influence. A considerable amount of work was done on the problem, but this simple method of experiment was ultimately abandoned in favour of a wind channel method. The principle employed is well known: the movement of the ions under the electric field is balanced by an opposing air blast. When moisture is present in the air stream several sources of error have to be guarded against, particularly electrical leakage over the surface of insulators. Zeleny in 1898 tried the air stream method. He employed a current of gas flowing through a tube, the end of which was fitted with a disc of gauze, which very nearly fitted it. He abandoned the method in favour of one in which the electric field on the ions was perpendicular to the air blast. This procedure has been followed by subsequent investigators. By making one modification in Zeleny's original method, we were able to adapt it for the determination of the variation in mobility with humidity. Instead of using a single piece of gauze to close the end of the tube, we divided it up into a central disc and a guard ring. The central disc was made a very accurate fit into the hole in the gauze, but was isolated electrically. Now it is a well-known fact that the velocity of the stream in the vicinity of the walls of a tube falls off to zero at the boundary. Consequently, the air-blast method fails if an attempt is made to work with the entire stream flowing through the tube, since there is no opposing blast to balance the electric field in the region of the walls. There is no difficulty in maintaining a constant stream of gas; we employed a small blower, and as indicator of the rate of flow a hollow sphere of glass floating in a conical tube fixed vertically. We found it impossible to blow a sphere with wall of uniform thickness, and this proved to be an advantage. It was observed that when the flowmeter was functioning the sphere would set itself with the thick lenticular segment lowermost. In this position it would ride quite steadily, remaining in the axis of the tube with a clear space all round for the air to flow past. A typical series of observations will be found on page 64 of the N.P.L. Report for 1926.

Now, for the purposes of practical hygrometry the use of a quadrant electrometer as a current measuring instrument is not feasible. By a valve amplification system we were able to obtain deflections of satisfactory magnitudes with changes of humidity on a sensitive pointer type of current indicator. What seems desirable, however, is a more powerful source of ionisation, as with high amplification of feeble currents surface leakages are apt to be troublesome.

Mr. R. S. WHIPPLE described a method, due to Prof. A. T. Mukarji, of Patna, for eliminating surface leakage in an electrometer. The whole of the apparatus is hermetically sealed in a dry enclosure and circuit changes are made by means of electromagnetic switches operated from outside the enclosure. Alternatively the apparatus might be so arranged that it can be manipulated from outside by means of permanent magnets.

Mr. J. H. COSTE said that the conductivity of cotton-wool was presumably due to mineral substances in the fibre, and as the ionisation of these varied with dilution the phenomena were complex. Further, the heating effect of the current would affect the water content of the fibre. He suggested the use of cellophane, which might be pleated and arranged between grid-shaped electrodes.

Mr. C. R. DARLING added that Cross and Bevan had found that whereas dry cellulose and pure water are non-conductors, moist cellulose has an appreciable conductance, as if cellulose had the power of ionising water.

Mr. D. N. MACDONALD said he was in search of a good method of indicating the disappearance of humidity in an evacuated space, in connection with a commercial process carried out in vacuo, in which the evolution of moisture continues until the process is complete, when it ceases.

Dr. EZER GRIFFITHS suggested that a dew-point method would be very sensitive; a silver thimble could be let into the chamber and cooled from outside the latter, while the dew on its convex surface inside the chamber could be observed through a window.

XIX.—ON A METHOD OF CONSTRUCTING THE CAUSTIC CURVE FORMED BY REFRACTION AT A PLANE SURFACE.

By C. J. Smith, *Ph.D.*, *A.R.C.S.*, Metallurgical Research Laboratory, University of Sheffield.

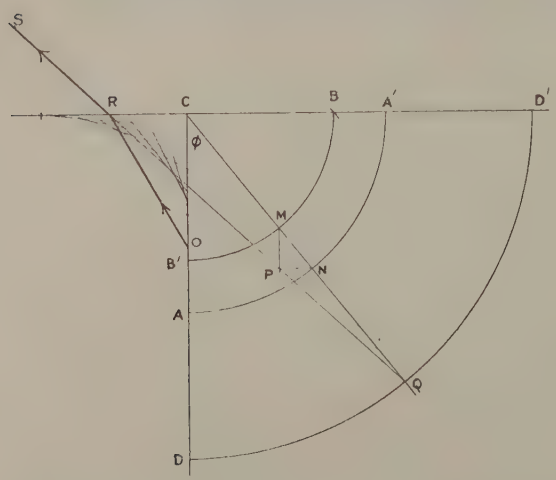
Received 25 *December*, 1927.

Abstract.

The Paper describes a convenient method of constructing the caustic curve in question. The method depends on the properties of an ellipse which cuts the rays orthogonally.

In teaching the elementary principles of light, a problem which is frequently given may be stated as follows: Assuming the refractive index of a medium to be μ, draw the caustic curve formed by the refraction of light which has its source at a point in the medium. If trigonometrical tables be employed, the subsequent procedure involves the construction of small angles, a somewhat difficult task if great precision is required. The alternative method of constructing the paths of light rays by drawing circles of radii whose ratio is μ involves a repetition of the construction for each refracted ray whose path is traced. The object of the present note is to give a method which is rapid and accurate.

It is a well-known theorem in geometrical optics that the rays which emerge from such a medium are normal to an ellipse whose focus is the luminous point and whose semi-major axis is μ times the distance of the point below the surface of separation of the two media.



The following property of an ellipse is now used to construct these normals. If the ellipse has semi axes (a, b), then the equation to the normal at the point "φ" is

$$ax \sec \varphi - by \operatorname{cosec} \varphi = a^2 - b^2$$

The intersection of this line with the line which defines φ, viz., $y = x \tan \varphi$, is the point $(\bar{x}, \bar{y})$, where

$$\bar{x} = (a+b) \cos \varphi$$

$$\bar{y} = (a+b) \sin \varphi$$

so that the locus of $(\bar{x}, \bar{y})$ is a circle of radius $(a+b)$ whose centre is at the centre of the ellipse.

Now let O be the luminous point at depth OC below the surface of separation of two homogeneous media. With C as centre and radius CA, where $CA=\mu CO$, construct an arc AA', and with O as centre and radius CA draw an arc to intersect the surface in B. Draw the arc BB' and also the arc DD' where $CD=CB'+CA$. Through C draw any right line $CMNQ$ where $A\hat{C}Q=\varphi$. If this line intersect BB' and AA' in M and N respectively, then parallels to the axes through these points give P, a point on the required ellipse, whilst PQ is the normal to the ellipse at the point P, so that the emergent ray is RS and the ray in the medium is OR. By variation of φ more rays can easily be constructed, and the envelope of QR is one half of the required caustic.

DISCUSSION.

Mr. W. R. Bower (communicated) : Mr. C. J. Smith has presented an interesting solution of an important problem in optics. His construction does not, however, fix the cusp of the caustic, nor the critical angle, and, like most methods, it is unfortunate with small angles.

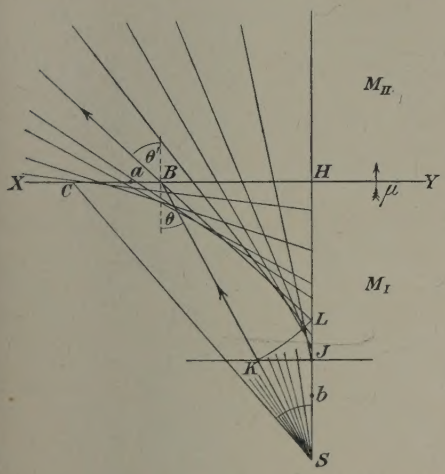
A description of another method is appended, one that is rapid and accurate and very simple, but so far as I know is not in common use.

Caustic by Refraction at a Plane Interface.—Let XY represent the plane surface separating media M_1, M_{11};

μ (supposed less than 1), the index of refraction from M_1 to M_{11};

S, a radiant in M_1;

H the intersection with XY of its normal through S.



Between H and S take J, so that $HJ=\mu\times HS$. Through J draw a parallel to XY.

Draw a ray from S incident at some point B, on XY and cutting the J-parallel at K. With B as centre, radius BK, draw a circular arc cutting SH in L. Draw LB, this is the refracted ray corresponding to SB. For

$$\mu=\frac{HJ}{HS}=\frac{BK}{BS}=\frac{BL}{BS}=\frac{BH}{BS}\Big/\frac{BH}{BL}=\frac{\sin\theta}{\sin\theta'}$$

θ and θ' are corresponding angles of incidence and refraction.

Similarly for other rays. The caustic appears as the envelope of the continuations of the refracted rays.

Also drawing shows that when B is close to H, L is very near to J, and J is the limiting position—cusp—when B is at H.

When L is at H, $BH/BS=\mu$, and the angle BSH is then the critical angle.

To find the limiting point of incidence C and the critical angle CSH; make $Ha=HJ$ and $ab=HS$. Draw SC parallel to ba.

For $aH=\mu xab$. $\quad\therefore CH=\mu . CS.\quad\therefore \sin CSH=\mu$.

The Caustic by Refraction at a Spherical Interface. may be obtained as an envelope as follows (no figure) : From a point N draw concentric circles of radii r (the surface), $\mu . r$, r/μ. From a radiant S draw any incident ray intersecting at B, Z, the circles of radii, r and $\mu . r$ respectively. Join NZ, intersecting the circle r/μ at Z'. Z,Z' are the aplanatic points. The line through BZ' is the refracted ray when BZ is the incident. Similarly for other rays through S in this meridianal plane (of the paper). By further construction points on the caustic are obtained. Ref., " A Graphic Method of Optical Imagery," Proc. Phys. Soc., Vol. XXV (1913), p. 176.

Mr. A. Adamson, lecturer in physics in the University of Manchester, also communicated the same construction as that given by Mr. Bower (above) for plane surfaces, and emphasised the simplicity of the proof and its suitability for presentation to elementary students.

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CONTENTS.

PAGE

XII. The Swan Band Spectrum of Carbon. By W. E. Pretty, A.R.C.S., B.Sc. 71

XIII. The Thirteenth Guthrie Lecture: The Electrodeless Discharge through Gases. By Sir J. J. Thomson, O.M., F.R.S. 79

XIV. Some Acoustical Phenomena Illustrated by Ripples—Transmission through Quincke Filters, Curved Conduits and Vibrating Partitions. By A. H. Davis, D.Sc. 90

XV. A Simple Graphic Method for the Determination of Galvanometer and Fluxmeter Constants, with a Note on the Measurement of Intense Magnetic Fields. By Allan Ferguson, M.A., D.Sc., and Eric J. Irons, B.Sc. 95

XVI. The Application of Electrical Resistance Measurements to the Study of the Atmospheric Corrosion of Metals. By John Christopher Hudson 107

XVII. Some Methods of Estimating the Intensities of Spectral Lines. By W. H. J. Childs, B.Sc. 132

XVIII. Electrical Methods of Hygrometry. By P. W. Burbidge, M.Sc., B.A. and N. S. Alexander, M.Sc. 149

XIX. On a Method of Constructing the Caustic Curve Formed by Refraction at a Plane Surface. By C. J. Smith, Ph.D., A.R.C.S. 156